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DEVELOPMENT AND PROCESSING
OF PYRRONE POLYMERS

by L. E. Karre, L. B. Keller, and L. J. Miller

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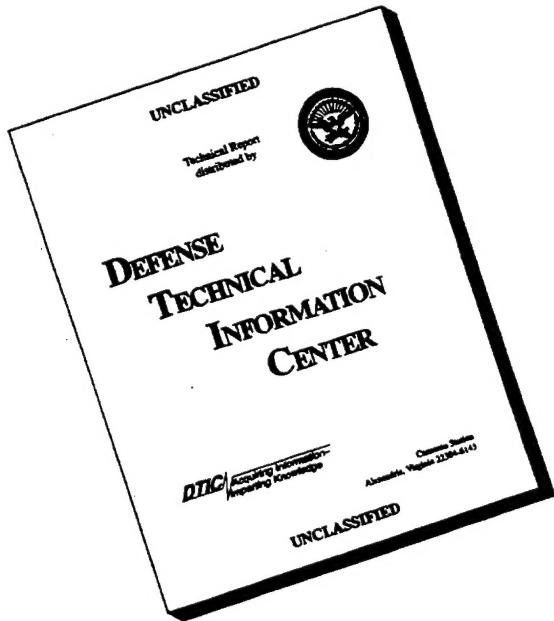
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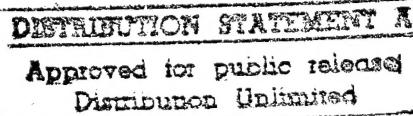
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

SUMMARY

This report describes the development and processing of Pyrrone polymers, that is, those polymers formed from the condensation reaction of aromatic dianhydrides with aromatic tetraamines in various solvents.

The work was divided into three consecutive phases based upon the type of dianhydride used and the solvent media in which the reactions were conducted.

In Phase I, the primary efforts involved the synthesis and characterization of the polymer formed from the condensation of pyromellitic dianhydride (PMDA) with diaminobenzidine (DAB) in polar solvents and the subsequent preparation and testing of fabricated articles. The synthesized ~~resultant~~ polymer gave disappointing strength properties which were attributed to the poor flow characteristics inherent in the polymer-solvent system.

In Phase II, primary efforts included the synthesis, characterization, and subsequent fabrication of the polymer formed from the condensation of benzophenone tetracarboxylic dianhydride (BTDA) with diaminobenzidine (DAB) in the esterifying solvent ethylene glycol (EG). Fiberglass laminates formed with the Phase II polymer had room temperature flexural strengths above 70,000 psi and moduli on the order of 5×10^6 psi. This improvement is attributed to several factors including the elimination of the ionic interaction between the polymer and polar solvents, the plasticizing effect of internally bound ethylene glycol, and the inherent increased flexibility of the additional BTDA single bond. The polymers synthesized in ethylene glycol, however, demonstrated relatively poor resistance to air oxidation at temperatures of 600°F.

Phase III of the program was initiated to investigate methods for improving the oxidative stability of the BTDA-DAB resin system. Primary efforts were directed toward the synthesis and improvement in thermal stability of laminates fabricated from the polymer formed from the condensation of BTDA with DAB in the esterifying solvent ethanol (EtOH). Laminates formed from this resin system also had

flexural strength above 70, 000 psi and moduli above 3×10^6 psi, but more important, the thermal stability was greatly improved as illustrated by the increased resin retention of the laminates.

The most promising resin system of the three investigated, from the standpoint of both mechanical strength and thermal stability, is the polymer formed from BTDA and DAB in ethanol.

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x

1.0 INTRODUCTION

Pyrrones, a new class of polymers developed at the NASA Langley Research Center, offer promise in present and future aerospace applications (ref. 1). The ladder-like structures of the aromatic heterocyclic polymers have a greater proportion of aromatic cyclic groups than any other developmental polymer.

Pyrrones may be formed from many cyclic dianhydrides and tetraamines under comparatively simple reaction conditions. Depending upon the starting materials used, two basic structures are obtained: the stepladder and the ladder polymers. In the stepladder form, the polyaromatic moieties are linked by single bonds. The ladder Pyrrone is linked by double bonds at each end of the basic Pyrrone unit to form a continuous double strand polymer.

During the initial phase of this program many of the unsuspected complexities in the development and optimization of this class of materials were uncovered. As information on polymer behavior was gathered, necessary changes in the synthesis and processing conditions of the resins were made. The resultant work on the development of this polymer system assumed the form of a three-phase program as progressive optimization was accomplished.

Phase I involved investigations primarily concerned with synthesis of the polymer in polar solvents, the characterization of this polymer system, and the development and optimization of techniques conductive to the fabrication of laminated parts (ref. 2). The coating, adhesive and dielectric properties of this polymer system also were briefly investigated. In Phase I most of the effort was concentrated on a polymer system consisting of the condensation products of pyromellitic dianhydride (PMDA) and diaminobenzidine (DAB) in either dimethylacetamide (DMAc), dimethylformamide (DMF) or N-methyl pyrrolidone (NMP).

The physical properties of laminated parts made from the Phase I polymer systems indicated that high strengths probably would not be achieved with the polymer system in its present form due to the poor

flow and molding characteristics inherent in the system. For this reason, the problem was circumvented by initiating Phase II of the program in which the polymer and solvent systems were changed.

In Phase II the basic polymer system consisted of the condensation products of benzophenone tetracarboxylic dianhydride (BTDA) and diaminobenzidine (DAB) in ethylene glycol (EG). This system is a stepladder type polymer because of the single bonds in both the BTDA and DAB molecules. In addition to the inherent increased molecular flexibility of this stepladder type polymer and the elimination of ionic interaction between polymer and solvent, the ethylene glycol appears to be bound chemically to the dianhydride in the polymer to give a molecular "plasticization." The expected increase in resin flow characteristics due to the increased polymer chain flexibility and internally bound solvent was indeed realized, since the strength values obtained from the Phase II polymer systems are approximately double those obtained for similar laminated parts in Phase I. Despite this improvement in strength properties it was found that the ethylene glycol type resins rapidly degraded in air at 600°F. For this reason, Phase III was initiated in an effort to improve the high temperature air stability of the resin system.

In Phase III the basic resin system consisted of the condensation product of the tetraethyl ester of benzophenone tetracarboxylic dianhydride (BTDA) and diaminobenzidine (DAB). Laminates formed from this resin system showed slightly lower mechanical strength properties than the ethylene glycol resin system, but the thermal stability at 600°F in air was markedly improved.

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2.0 PYRRONE CHEMISTRY

The Pyrrones are a class of heterocyclic aromatic polymers having the following moiety as a recurring unit in the polymer chain:
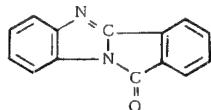
This type of polymer was prepared by Bell and Pezdirtz under the name polyimidazopyrrolones or Pyrrone (ref. 3, 4, 5, 6). Other researches in this field including Dawans and Marvel, referred to these polymers as polybenzimidazolimides (ref. 7) while Colson, Michel and Paufler referred to this class of polymers as polybenzoylenebenzimidazoles (ref. 8).

Pyrrones generally have been synthesized by the reaction of aromatic dianhydrides with aromatic tetraamines. The reactions are illustrated by the typical equations shown below for pyromellitic dianhydride (PMDA) and 3,3'-diaminobenzidine (DAB).

PMDA   DAB

I (A-A-A)

$-H_2O$ $-H_2O$

II   III

$-H_2O$ $-H_2O$

IV
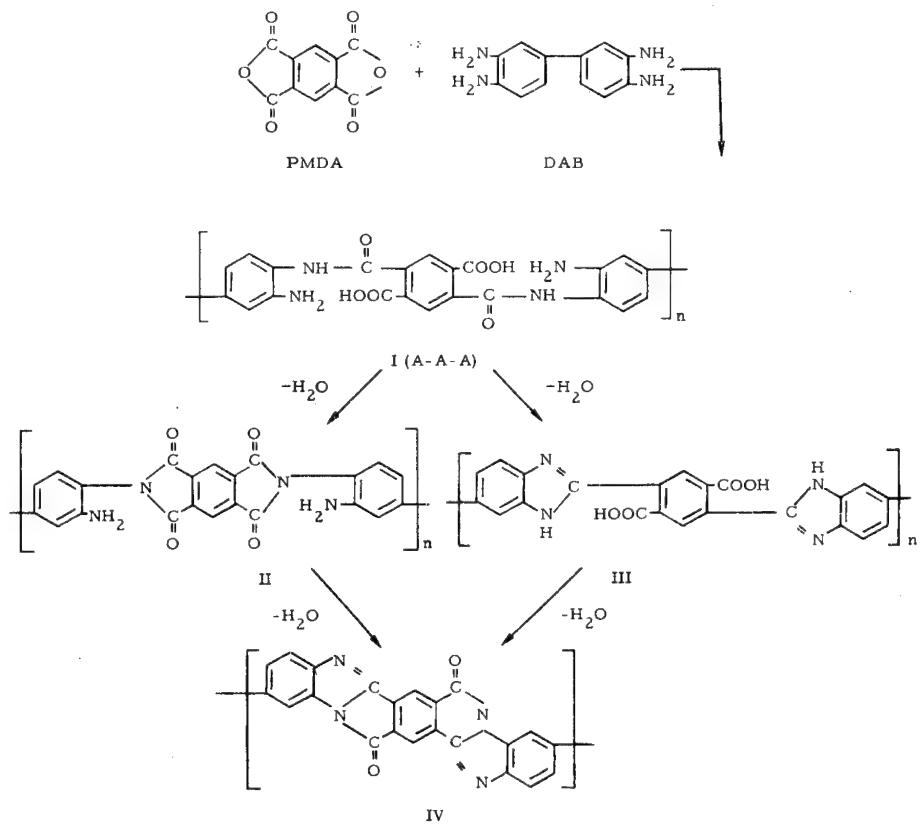
Several isomeric structures are possible for each of the indicated types of polymers. The initial reaction product (I) is a polyamide which undergoes two successive condensation reactions to form the Pyrrone (IV). Two main routes to the fully cyclized polymer are possible. Colson, Michel and Paufler found that the preferred route at temperatures between 130 - 150°C led to the formation of the polyimide (II), while others (ref. 4, 7) found evidence for the involvement of both polyimide and polybenzimidazole (III) intermediates.

Although the Pyrrone (IV) is insoluble, the amino-acid-amide (A-A-A) polymer (I) dissolves readily in such solvents as N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF), from which strong, but brittle, films can be cast. Cyclocondensation to convert (I) to (II) occurs at about 130 to 150°C in a film, and further condensation to form IV takes place above 200°C, with temperatures as high as 250°C required for complete conversion (ref. 8).

One reason for the interest in Pyrrones is the possibility of forming ladder polymers, which theoretically should possess a considerable advantage over single-stranded polymers in terms of stability to radiation and heat. Such a ladder polymer can be formed (ref. 3, 4, 5, 7, 8) from pyromellitic dianhydride (PMDA) and 1,2,4,5-tetraaminobenzene (TAB).

PMDA   TAB

V
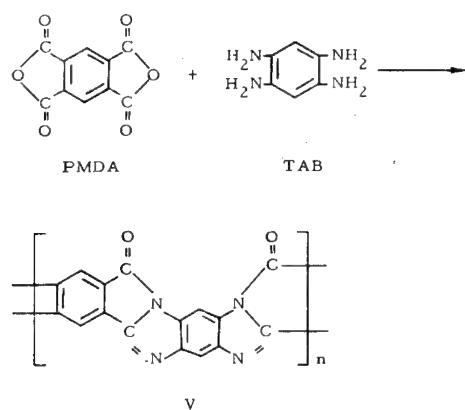
Most of the known Pyrrone polymers, however, have only a partial ladder structure and have been dubbed "stepladder" polymers (ref. 1, 3, 4, 5).

These polymers are exemplified by polymers (IV) and (VI), the latter being derived from 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride (BTDA) and DAB.

BTDA   DAB

VI
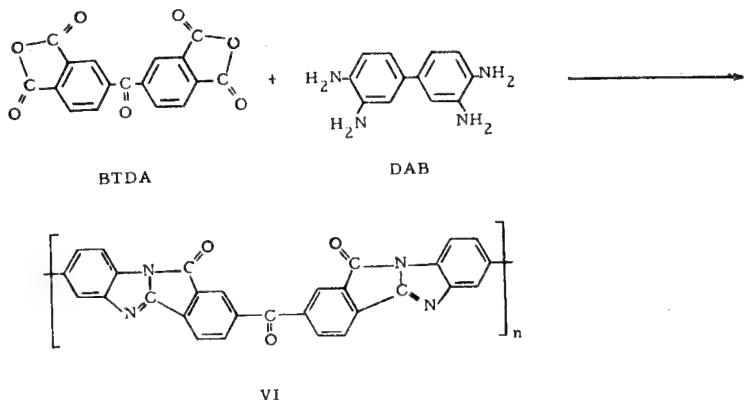
The nature and extent of crosslinking may have a significant effect on the properties of the cured product. Simple crosslinks probably do not exist to a great extent, but a three-dimensional polymer can result from extensive branching. Two types of stable branching seem likely to be present, one involving imide linkages (VII) and the other having imidazole groups (VIII).

VII

VIII

5
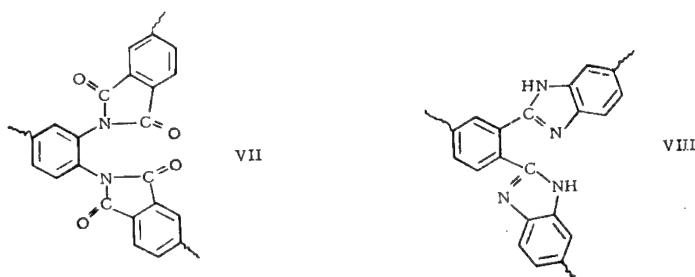
Gelation of the A-A-A polymer (I) occurs quickly in solution when a slight excess of dianhydride is added, but not when an excess of tetraamine is present (ref. 8). Amide crosslinks (as shown in IX) are the cause of this gelation, since the amide groups are formed only with anhydride and not with the much less reactive carboxyl groups. These crosslinks would appear to be conducive to the formation of imide branches or crosslinks of the type shown in (VII) and (X).

I (A-A-A)   PMDA

IX

heat
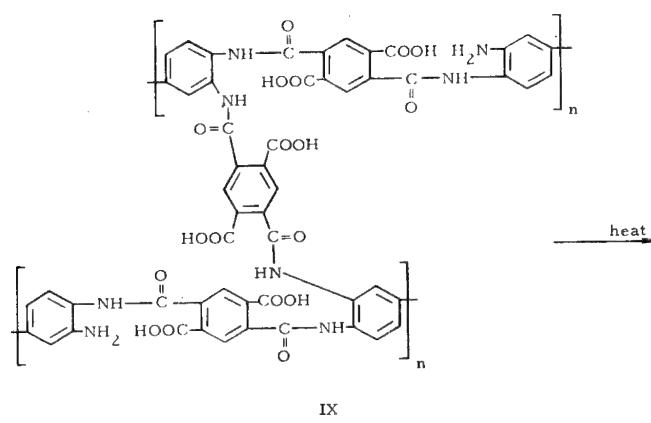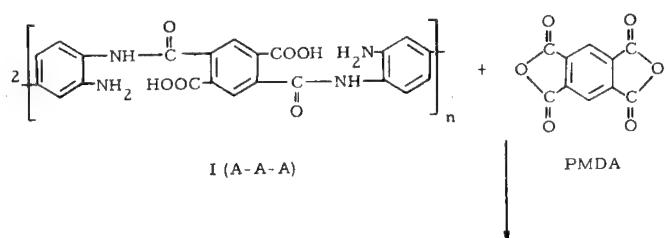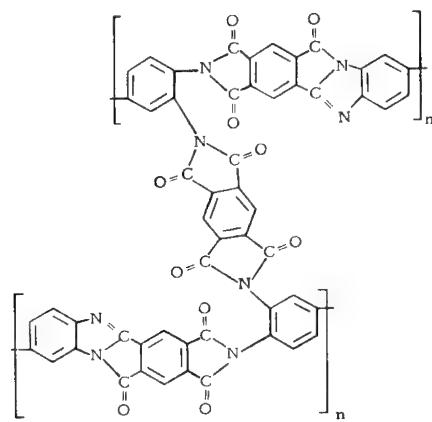
X

Using phthalic anhydride and o-phenylenediamine as model compounds, however, Dawans and Marvel found a tendency to form branches of the type indicated by (VIII) and reported none of the type shown in (VII).

Pyrrone polymerizations have been carried out both in a melt and in solution. Preferred solvents have been DMAc, DMF, dimethyl sulfoxide (DMSO), and polyphosphoric acid, but bis(2-methoxyethyl) ether (diglyme), phenol, and pyridine have also been used. Strong bonding between the polymer and the solvent (ref. 3, 4, 5) as well as between the polymer and moisture from the air (ref. 6) has been noted. Interaction between the monomers and certain solvents is also likely. This program has revealed that the solvent can exert an extremely important effect on the strength of the formed and cured composite.

With few exceptions, the monomers always have been the dianhydride and the tetraamine or the tetraamine tetrahydrochloride. Bell and Jewell have reported using 2,5-dicarbomethoxyterephthaloyl chloride in place of PMDA with no apparent change in polymer properties. Free tetracarboxylic acids were reacted with tetraamines to prepare polybenzimidazobenzophenanthrolines, a class of polymer which is related structurally to the Pyrrones (ref. 9, 10). Pyrrone synthesis in phenol (ref. 7) almost certainly proceeds in part through phenyl ester intermediates, although this was not specifically mentioned in the report by Dawans and Marvel.
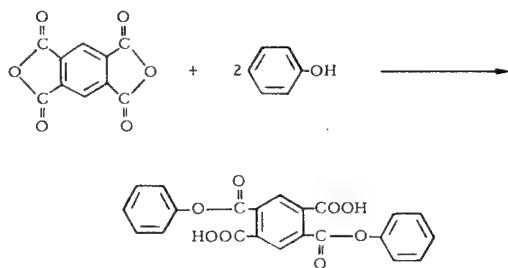
A prior interaction between the monomers and other solvents is also conceivable, and such reactions would alter the actual monomers.

In Phase I of this program it was observed that the solvent-free polymer was infusible and that adequate flow could be obtained during cure only by allowing some solvent to remain in the polymer for the molding process. Infusibility of the polymer, which was actually the amino-acid-amide (A-A-A) polymer, was attributed to the strong electrostatic attractions between the ionic sites on the zwitterionic forms of the A-A-A polymer. For the A-A-A polymer derived from 3, 3'4, 4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3, 3'-diaminobenzidine (DAB) this ionic structure is indicated by (XI).

XI
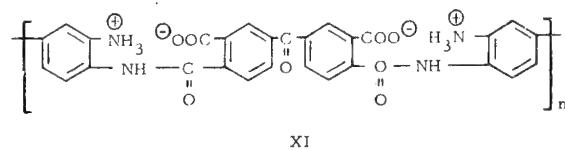
In order to avoid the formation of an ionic polymer it was decided to employ tetracarboxylic acid derivatives other than the dianhydrides. Esters and imides were suggested as being useful monomers for this purpose, the anticipated reactions follow.

XIII

−H₂O

XIV

−ROH

VI

3,3',4,4'-benzophenonetetracarboxylic
diimide

DAB

XV

−NH₃

−H₂O

XIII

−H₂O

XVI

−NH₃

VI
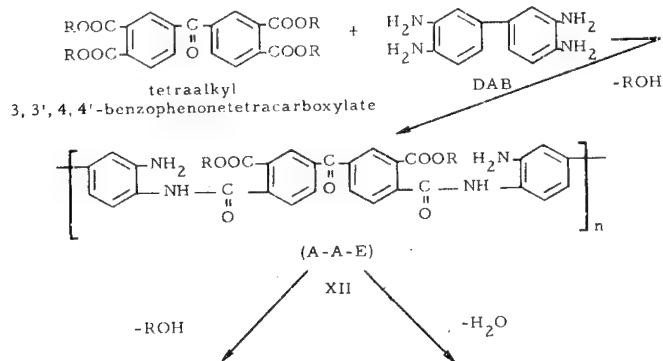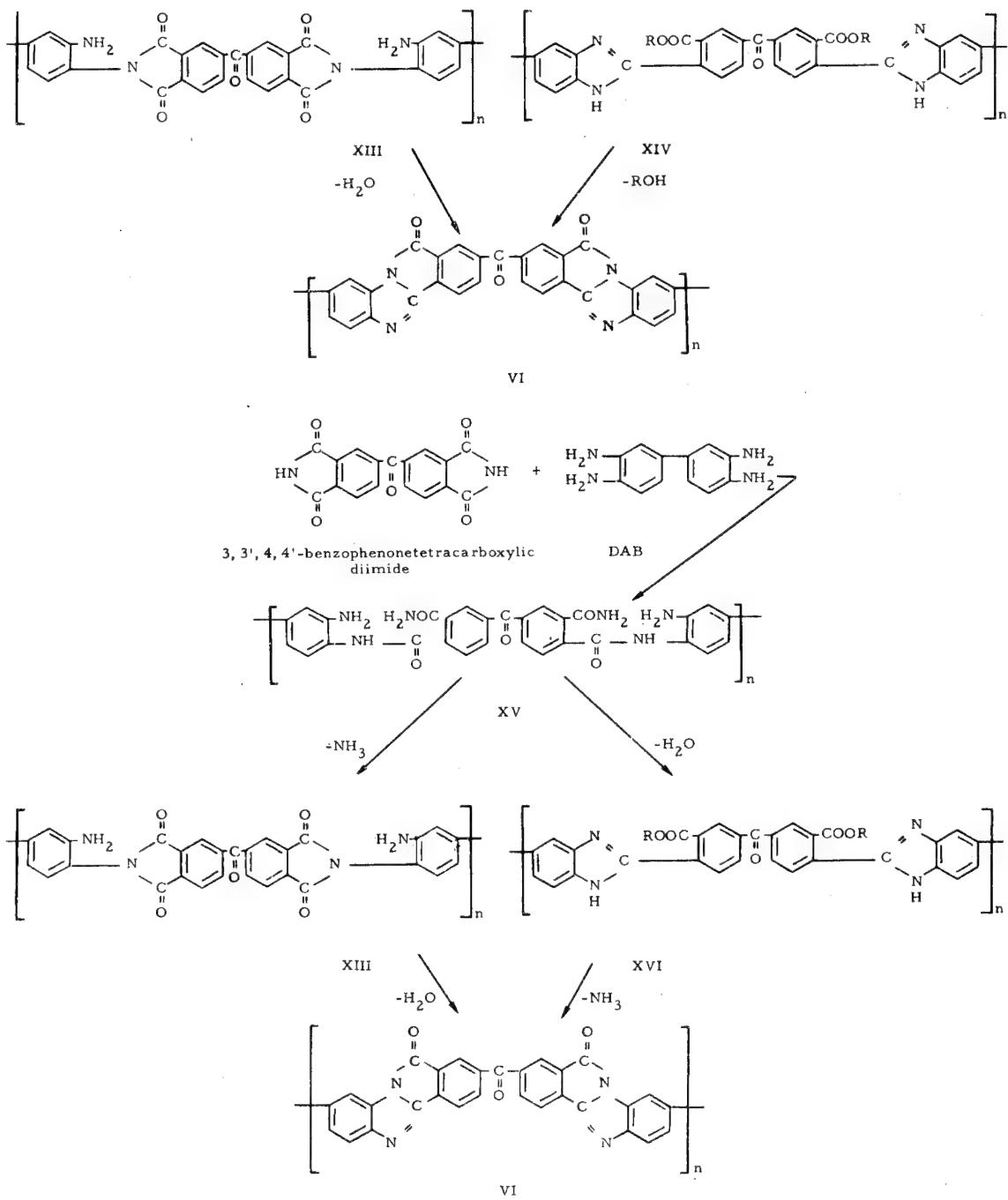
Instead of the A-A-A polymer, the derivatives (XII and XV) of
the A-A-A polymer are obtained, and the -COOH groups are replaced
with the neutral -COOR or -CONH$_2$ groups. Both processes can pro-
duce the same polyimide (XIII) as that obtained by starting with the
dianhydride, but different polybenzimidazole derivatives (XIV and XVI)
are formed. Theoretically, all processes eventually lead to the same

Pyrrone (VI). However, none of the intermediates are ionic when the original monomer is either the imide or the tetraester.

The nonionic character of the intermediates was expected not only to improve the flow properties of the polymers during cure but also to enhance their solubility in less polar solvents. Solvents less polar than DMAc should be more easily removed than DMAc, and the problem of hydrolysis of the bound DMAc could be avoided. Of the two possible nonionic intermediates (XII and XV), the amino-amide-ester (A-A-E) polymer (XII) was preferred since esters generally have lower melting points than amides.

Exploratory work at NASA-Langley Research Center indicated that improved Pyrrones could be obtained by preparing the polymers in ethylene glycol. Therefore, Phase II was undertaken as a study of the use of esters as monomers, with heavy emphasis placed on the esters of ethylene glycol. A concentrated effort also was devoted to the esters derived from BTDA rather than PMDA because of the added flexibility imparted to the polymer by the $-\overset{\overset{\text{O}}{\|}}{\text{C}}-$ linkage. Increasing the flexibility of a polymer ordinarily makes it more soluble and fusible.

The polymers derived from the ethylene glycol esters demonstrated improved mechanical strength properties, however, their long term thermal stability fell somewhat short of that expected. Thus, the study of the polymer derived from the ethyl alcohol ester of BTDA was initiated to determine whether the type of alcohol selected would improve the thermal stability of the polymer. In Phase III the major emphasis was placed upon improved thermal stability rather than on mechanical strength properties.

3.0 PHASE I - POLYMERS IN POLAR SOLVENTS

The evaluation of the materials produced in Phase I is based upon the behavior during polymer synthesis (Section 3.1), characterization of the resins (Section 3.2), the physical properties of laminates (Section 3.3), and additional studies on moldings, coatings and precipitated powders (Section 3.4). The conclusions drawn from the Phase I investigation are presented in Section 3.5.

3.1 POLYMER SYNTHESIS

Establishment of satisfactory reaction conditions to prepare developmental quantities of Pyrrone polymers from PMDA and DAB and from BTDA and DAB was the objective of the synthesis effort. In general, the experimental approach of Phase I closely followed procedures developed by Bell and Pezdirtz (ref. 3, 4, 5).

Most of the experimental resins were prepared from PMDA and DAB in DMAc. Commercial PMDA was sublimed in 2-pound batches prior to use, and the DAB was used as received. DMAc was carefully dried for some experiments, although commercial technical grade at first was considered to be satisfactory without further purification and large quantities of resin were prepared in this unpurified solvent.

The reactions were carried out by adding a solution of the anhydride to a vigorously stirred solution of the tetraamine in a Waring blender. The apparatus was contained in a polyethylene bag which alternately was evacuated and flushed with argon to displace the air prior to the start of the reaction.

A few small-scale experiments were performed first in a very small Waring blender to develop suitable methods for handling the reaction. In these preparations 95 percent of the theoretical quantity of PMDA was added to the DAB in one portion, and additional PMDA solution then was added dropwise until a desired viscosity was achieved. It was noted, however, that gel particles formed within seconds after only the first portion of PMDA solution was added, regardless of the rate of addition. This premature gelation was attributed to local

excesses of PMDA in the mixture which resulted from inadequate stirring in the small size blender. When the reaction was conducted in a larger blender, which provided more rapid mixing, gelation was virtually eliminated until an excess of PMDA was present.

Samples of the reaction mixture were drawn up into a tube periodically, and the viscosity was determined by measuring the time required for a steel ball to drop through a given column of solution. Figure 1 shows a plot of the drop time for the steel ball as a function of the number of drops of PMDA solution added after the initial 95 percent of the theoretical amount of PMDA had been combined with

INITIAL MIXTURE CONSISTED OF 0.0200 MOLE OF DAB AND 0.0192 MOLE OF PMDA, APPROXIMATELY 10 PERCENT IN DMAC. MIXTURE WAS TITRATED WITH ADDITIONAL PMDA SOLUTION (ONE DROP EQUIVALENT TO 1.06×10^{-5} MOLES OF PMDA). TIME INDICATED IS THAT REQUIRED FOR STEEL BALL TO FALL THROUGH GLASS TUBE FILLED WITH RESIN.

EQUIVALENCE POINT
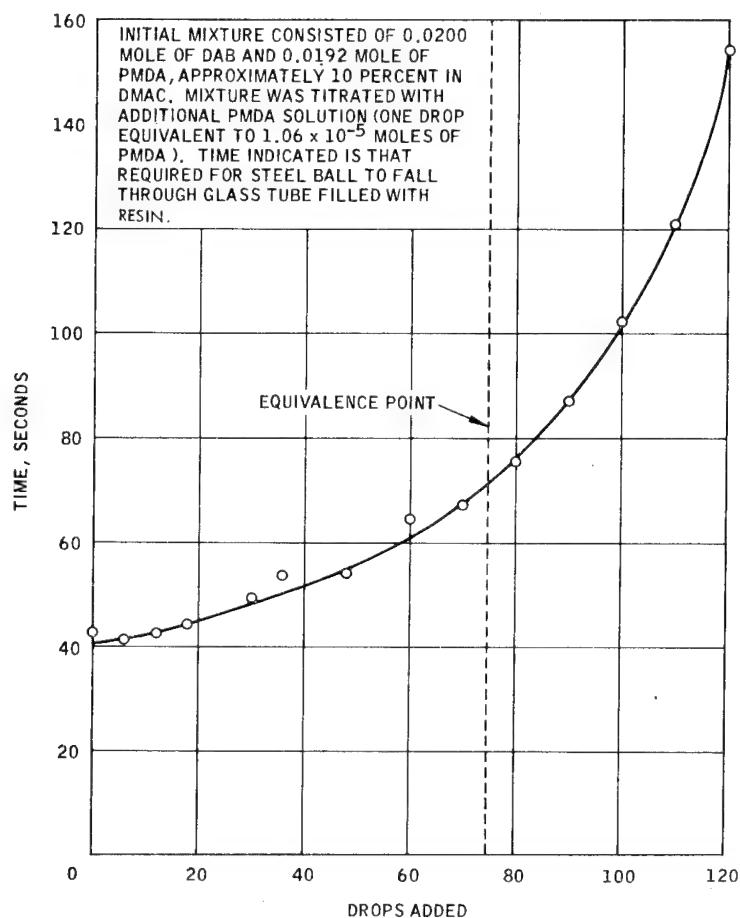
Figure 1. Viscosity Curve of PMDA-DAB
Resin Near Endpoint
of Reaction

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the DAB. As can be seen from the shape of the curve in Figure 1, the appropriate endpoint was not obvious, and no sudden changes in viscosity occurred.

The reaction was exothermic, and the heat of reaction plus the heat introduced by stirring quickly raised the temperature from ambient to about 55°C. Efficient cooling methods appeared desirable.

After the initial experiments the preparation was scaled up and run in a 1-gallon Waring blender equipped with a water-cooled base and an internal cooling coil. A large water bath controlled at 25°C was used as a source of cooling water. Excessive cooling seemed to slow the reaction to an undesirable extent; thus, after two runs with efficient cooling it was decided to allow the temperature to rise as high as 50°C. The higher temperature was important particularly when the viscosity of the solution was used to indicate the end point of PMDA addition. If this end point was determined at 25°C, the amount of PMDA added was actually an excess, and the resin gelled during storage. However, if this end point was determined at 50°C, the reaction essentially was complete at the time of titration, and the excess of dianhydride and the resulting gelation were avoided.

Gel formation was minimal in the 1-gallon container. In one instance the gel was isolated by filtration, dried, weighed and found to comprise 0.27 percent of the solids by weight. This gel was produced from a reaction of equivalent molar quantities of PMDA and DAB.

In all cases, the resins did not have the same viscosity even when the preparative methods seemed to differ only in unimportant details. A pH value was determined occasionally for the resulting resin, although the significance of a pH measurement in DMAc is not certain. These pH values also varied considerably, falling in the range between 3.9 and 5.5.

Since the viscosity did not indicate a sharp end point, the concept of titrating to a viscosity end point with the last portion of PMDA solution was abandoned. Subsequently PMDA and DAB were combined in equal molar proportions.

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Following several exploratory preparations in the 1-gallon blender, a series of preparations was undertaken to provide a 10-gallon master batch of resin (J-1). The viscosity of the J-1 resin was determined at various temperatures using a Brookfield LVF 1 at 60 rpm — number two spindle. The results are shown in Figure 2 which depicts a typical viscosity temperature curve.

The resulting resins were blended in a storage tank, then concentrated by evaporation in a rotary still to a calculated solids content of 20.4 percent. J-1 resin had an intrinsic viscosity of 0.41. The pH of the DMAc solution was 3.9, the lowest of the pH values measured.

The low flexural strength of laminates fabricated from resin J-1 was a disappointment (see Section 3.3). In part this could be attributed to the poor flow properties of the resin. However, an odor of acetic acid was always present when the resin was processed, suggesting that substantial quantities of solvent (DMAc) remained strongly bound to or trapped in the resin during cure, and that this solvent hydrolyzed to yield acetic acid. Water for the hydrolysis could be furnished by the
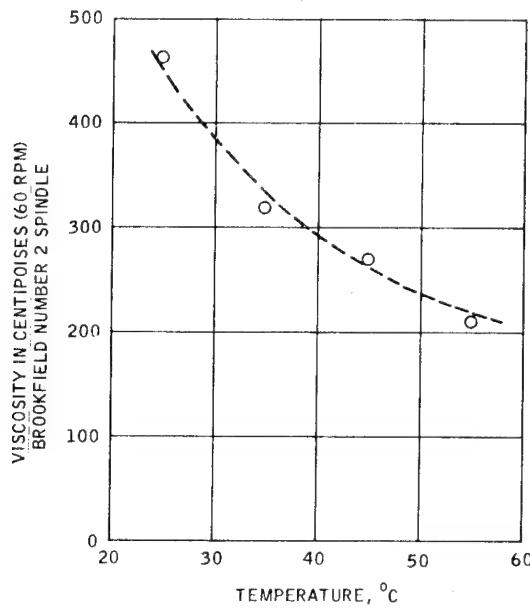
Figure 2. Viscosity of J-1 Resin as Function of Temperature

cyclocondensation of the polymer. The possibility existed, therefore, that the bound solvent was responsible for poor polymer properties. This bound solvent increased the void content of the cured products. Moreover, chemical reactions of the following type might occur:

$$CH_3C-N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \ + \ H_2O \longrightarrow CH_3COOH \ + \ H-N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$$
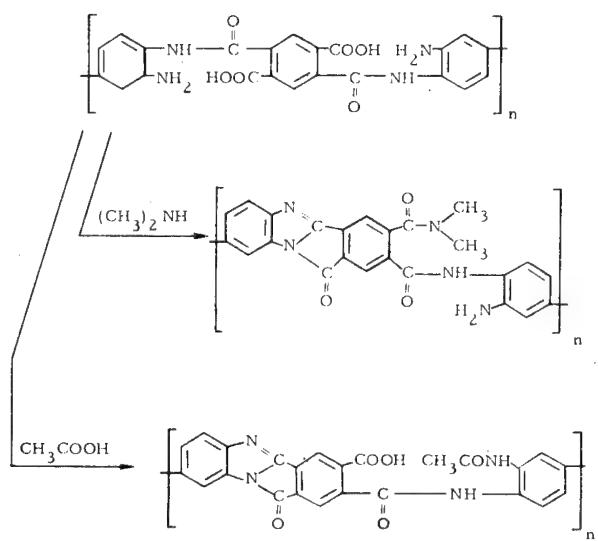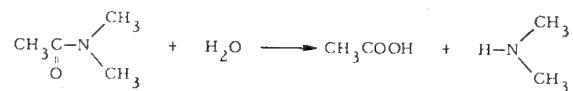
Some of the reaction products may inhibit or prevent the curing reactions.

In response to these developments, two new approaches were undertaken. First, both reagent grade and technical grade DMAc were purified further by distillation from phosphorus pentoxide and treatment with a molecular sieve. Resins were prepared in the purified solvents and were used to prepare test specimens. The odor of acetic acid was no longer detected during the fabricating operation and the finished parts were superior in appearance to previous laminates, but the flexural strengths were scarcely altered. Polymers with slightly lower intrinsic viscosities were obtained in the purified DMAc than in the technical grade solvent.

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The second approach eliminated DMAc entirely and used DMF and N-methyl-2-pyrrolidone (NMP) as the solvent. Spectrographic grade DMF was dried on a molecular sieve column prior to use. Technical grade NMP was fractionated, then distilled from phosphorus pentoxide and passed through the molecular sieve column. Resins were prepared in these solvents by essentially the same procedure used for the DMAc resins.

Portions of polymer were precipitated from the DMAc resins with water and acetone. Precipitation with water was unsatisfactory because the polymer retained a substantial quantity of residual DMAc. The polymer precipitated with acetone was an infusible, fine yellow powder which turned light green in air and which was readily resoluble in DMAc, DMF, NMP, and DMSO. These polymer samples were used for differential thermal analyses and for molding specimens of pure resin.

Resins with only a 2-percent concentration of solids were also prepared in purified DMAc and tested because it was recognized that the A-A-A polymer has a zwitterionic structure (XVII) rather than the nonionized structure (I). The ionic character of the polymer
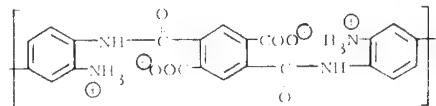
XVII

produces strong intermolecular attractions which may cause the polymer molecules to be closely associated in concentrated solutions. Closely associated polymer molecules may undergo branching reactions during the polymer preparation, and the branches may inhibit complete cyclization to the Pyrrone structure. To minimize this possible tendency toward branching, the polymer was prepared in a more dilute solution in which the polymer molecules should be more isolated from each other. Polymers prepared in dilute solutions had lower intrinsic

viscosities, but after concentration of the resin and fabrication of laminates, the final products were essentially the same as those derived from concentrated solutions.

A resin sample also was prepared from BTDA and DAB in DMAc. The procedure was similar to that for the PMDA-DAB syntheses.

3.2 POLYMER CHARACTERIZATION

As work progressed throughout Phase I it became apparent that the PMDA-DAB resins in the polar solvents (DMAc, DMF and NMP) could not be expected to produce laminates with flexural strengths much better than 40,000 psi and moduli much over 3 million psi. Since appropriate fabrication techniques were used, it is believed that the reason for the formation of mediocre laminates was in the basic resin system rather than in the laminating techniques. Some of the latter laminates prepared toward the end of Phase I were made with resins that were synthesized in highly purified and carefully dried solvent, but no marked improvements in physical properties were evident. The presence of impurities in the solvents, although detrimental, was not the prime reason for the comparatively low physical properties. If the polymers were not sufficiently solvated, i.e., the solubility of the polymer in the resin solvent was poor, this would be indicated by intrinsic viscosity data. With this in mind, a series of intrinsic viscosity measurements was conducted on the resins that had been synthesized in the different types of solvents.

Reduced viscosity versus concentration data were developed for a series of the resins synthesized in Phase I. The viscosity data were obtained for the resins prepared in various solvent systems. All viscosity data were developed with an Ostwald-Fenske viscometer at a constant 25°C temperature.

The pertinent information was obtained by examination of the intrinsic viscosity data and the shape of the reduced viscosity versus concentration curves. Both polymers which were synthesized in dried reagent grade solvents exhibited curves typical of polyelectrolytes in

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solution. As the resins were diluted to lower concentrations (below 0.2 gram/100 ml) the curves rose rapidly and appeared to be approaching the zero concentration axis asymptotically. This behavior was drastically reversed in the case of the acidified resin which exhibited the highest intrinsic viscosity yet had the low concentration portion of the curve approaching the origin. This increased intrinsic viscosity upon addition of the electrolyte (HCl) indicates that the increased concentration of anionic and cationic counter-ions tends to suppress the formation of an infinite network. Those polymers synthesized in purified technical grade solvents exhibited behavior similar to that of the acidified resin except that lower intrinsic viscosities were obtained. This appears to indicate that the "purified" solvents contained enough impurities to act as counter-ions in suppressing gel formation but were still relatively poor solvents. The relatively low intrinsic viscosities of the cold run and dilute runs were probably due to a combined effect involving both counter-ions plus lower molecular weights as a result of a low degree of polymerization caused by low temperatures and dilution.

To further characterize the behavior of resins in polar solvents an attempt was made to determine the relative dynamic modulus as a function of temperature.

It was found feasible to coat a 3/32-inch diameter cylindrical steel rod with resin for dynamic modulus measurements. Previous attempts to coat thin beryllium-copper strips with the resin were unsuccessful since cracking of the resultant film always occurred at sharp corners during drying. One steel rod was given eight coatings with NASA Pyrrone resin No. M-11 which gave an average film thickness of 5-6 mils. At this point, the remainder of the M-11 resin gelled completely preventing further coating.

Vibrating Reed Analysis of a high solids (~50 percent) J-1 resin in DMAc was undertaken. A three-ply laminate of E glass and resin, previously cured out at 1000 psi at 600°F, was employed as the supporting substrate. A 1/2 x 3-inch strip of substrate was subjected to a temperature cycle of 75-500°F. The apparent modulus E_{app} was found to be linear with temperature.

The inert substrate was coated with a high solids resin (concentrated by vacuum evaporation at room temperature) and its apparent dynamic modulus monitored. The coating was approximately 6 mils thick and adhered well to the substrate. The temperature was held at 100°C during the cure phase of the investigation. The resin became glassy, and the modulus remained constant after approximately 110 minutes.

The temperature controller was set at 270°C, and both heating elements activated. The temperature rose from 100 to 270°C in 40 minutes. During this period the relative modulus was observed at selected temperatures.

At a constant temperature of 100°C, the first 75 minutes of cure are a combination of solvent removal and some condensation reaction. From 75 minutes to about 110 minutes it appears that the change of modulus is due principally to further condensation of acid-amino groups. At about 110 minutes the resin is in a glassy state and thus prevents any main chain crankshaft rotation. Restriction of this mode of rotation prevents further condensation from occurring. It is probable that the restriction to main chain rotation is due to intermolecular forces which are abundantly present in the A-A-A polymer and perhaps to some three dimensional crosslinking.

When the change of relative modulus with temperature is plotted, the initial section of the curve is linear with temperature thus yielding a constant dE_{rel}/dT up to 175°C. At this temperature a sudden jump in modulus is observed which is apparently associated with the condensation to the amine-imide. At about 210-215°C an additional modulus increase is observed that is probably indicative of further condensation to the Pyrrone structure.

Stainless steel substrates were coated with J-1 resin and PMDA-DAB resin synthesized in DMAc. One of the coated substrates was used in an effort to determine the relative dynamic modulus of the polymer as a function of temperature. The coated substrate was heated from ambient to 300°C while monitoring the fundamental frequency of vibration. No appreciable change in modulus was detected.

In an attempt to further characterize the polymers formed in polar solvents without the effect of the solvent, it was decided to precipitate the polymer from DMAc followed by washing and drying operations. These pure polymers then could be used for differential thermal analysis and molding studies.

Initial attempts to precipitate the polymer with water were unsuccessful. The precipitation was done in the 1-gallon blender using 400 ml of H_2O to 100 ml of J-1 resin. After 5 minutes of agitation the slurry was allowed to settle for 1 hour. The pH of the decantant was acidic as measured with litmus paper. The filtered slurry of polymer was dried in a rotary still at 55°C. The polymer fused, indicating high residual DMAc.

The polymer was successfully precipitated by blending 100 ml of J-1 resin with 300 ml of acetone in a blender, washing several times, filtering and drying under vacuum. The polymer powder produced by acetone extraction is a fine golden yellow powder. Upon exposure to air the surface layer turns light green. The powder is soluble at 10 percent concentration in dimethyl acetamide, dimethyl formamide, N-methyl-2-pyrrolidone and dimethyl sulfoxide. The polymer is essentially insoluble in piperidine.

Differential thermal analyses were run on three powdered polymers obtained by precipitation in acetone. The polymers tested were recovered from J-1 resin (technical DMAc), D1516-29X resin (purified reagent grade DMAc) and D1516-29Y resin (purified technical grade DMAc). All tests were run in a nitrogen atmosphere from ambient to 850°C at a heating rate of 10°C/minute.

All three of the precipitated polymer powder samples behaved similarly and showed initial endothermic character probably due to loss of indeterminate volatiles. In the 120-170°C temperature range the materials begin to exhibit exothermic behavior which continues to the 610-650°C range. This exothermic behavior is relatively

broad and not well defined and is most probably due to the curing mechanism. No well defined optimum curing temperature could be determined from the DTA curves. Endothermic decomposition appears to begin in the 600-650°C temperature range.

3.3 LAMINATING AND PHYSICAL PROPERTIES

Criteria for the development of satisfactory laminates were the flexural strength and modulus that could be achieved with a particular resin system. Once a resin system showed promise as a laminating material, it was tested further to see if it were also a high temperature stable material. The results of these laminating studies for Phase I of the program are summarized in Tables I and II.

The first laminates recorded are the PF-14 series. The earlier series of laminates were part of a familiarization program; thus, no significant results were obtained for laminates PF-1 through PF-13. These laminates were formed using several resins submitted by NASA Langley (designated N-4 and M-11) plus several experimental resins synthesized at Hughes.

Examination of Table I indicates that all laminates were formed using a standard reinforcement (with the exception of PF-21 where CCA-1 carbon cloth was used). The standard reinforcement selected for the lamination studies was 181 glass cloth with an A1100 finish. By using a standard reinforcement material, this variable could be controlled until the time that optimization of the reinforcement was desired.

All resins used in Phase I were of the PMDA-DAB-polar solvent type except the resin used to prepare laminate PF-38, which was of the BTDA-DAB type in N, N, dimethylacetamide (DMAc). The various PMDA-DAB resins were in one of three solvents, DMAc, N-methyl-2-pyrrolidone (NMP) or N, N, dimethylformamide (DMF). The majority

Table I. PMDA-DAB-DMAc Laminate Properties for Phase I Program

Laminate Designation (1)(2)	Laminating Conditions			Final Resin Content, percent	Density, gm/cc	Volume Percent Voids in Resin, percent	Average Flexural Strength (psi x 10^{-3})		Average Modulus (psi x 10^{-6})		Remarks
	Contact Time, minutes	Maximum Pressure, psi	Maximum Temp, °F				Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	
PF14-1 [3]	0	500	200	–	–	–	16.7	–	1.29	–	–
PF14-2 [3]	0	500	300	–	–	–	21.8	–	1.42	–	–
PF14-3 [3]	0	500	400	–	–	–	23.1	–	1.44	–	–
PF14-4 [3]	0	500	500	–	–	–	16.1	–	1.35	–	–
PF14-5 [3]	0	500	600	–	–	–	16.6	–	1.38	–	–
PF15-1	–	50	600	15.8	1.59	60.0	37.0	22.1	1.74	1.52	Laminate formed by vacuum bag technique
PF15-2	–	50	600	15.8	1.56	61.0	34.0	18.9	1.66	1.35	Laminate formed by vacuum bag technique
PF16-1	5	2000	600	25.0	1.56	45.0	37.0	–	1.66	–	–
PF16-1A [4]	5	2000	600	25.0	1.56	45.0	11.7	–	1.49	–	–
PF16-2	5	5000	700	24.0	1.70	37.0	32.9	–	2.24	–	–
PF17	0	1000	750	30.5	1.82	16.5	39.7	–	2.29	–	–
PF18-1	0	500	650	23.0	1.52	50.5	29.1	–	1.91	–	No elevated temp. testing was conducted
PF18-2	0	500	700	24.0	1.54	49.5	28.7	–	2.07	–	No elevated temp. testing was conducted
PF18-3	0	500	750	23.0	1.50	52.0	27.9	–	1.96	–	No elevated temp. testing was conducted
PF18-4	0	2500	650	25.0	1.66	39.0	29.5	–	2.14	–	No elevated temp. testing was conducted
PF18-5	0	2500	700	23.0	1.72	37.6	31.6	–	2.30	–	No elevated temp. testing was conducted
PF18-6	0	2500	750	24.0	1.71	47.6	34.9	–	2.49	–	No elevated temp. testing was conducted
PF18-7	0	5000	650	25.0	1.70	35.0	30.5	–	1.93	–	No elevated temp. testing was conducted
PF18-8	0	5000	700	23.0	1.74	36.5	29.9	–	2.11	–	No elevated temp. testing was conducted
PF18-9	0	5000	750	23.0	1.80	32.0	36.7	–	2.69	–	No elevated temp. testing was conducted
PF19	–	200	350	–	–	–	–	–	–	–	Laminate formed by vacuum bag technique
PF20	0	500	600	–	–	–	41.0	–	3.10	–	No elevated temp. testing was conducted
PF21 [5]	0	1300	600	–	–	–	10.6	–	1.37	–	No elevated temp. testing was conducted

(1) All PMDA-DAB resins were in DMAC solvent
(2) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish with the exception of PF-21

(3) Laminates PF-14-1, 2, 3, 4, 5 were postcured at 600°F for 2 hours in air
(4) Laminate PF-16-1A was postcured at 600°F for 72 hours in air
(5) Laminate PF-21 was fabricated with CCA-1 carbon cloth reinforcement

Table II. PMDA-DAB and BTDA-DAB Laminate Properties for Phase I Program

| Laminate Designation (1) | Resin Designation | Laminating Conditions | | | Final Resin Content, percent | Density, gm/cc | Volume Percent Voids in Resin, percent | Average Flexural Strength (psi x 10⁻³) | | Average Modulus (psi x 10⁻⁶) | | Remarks |
		Contact Times, minutes	Maximum Pressure, psi	Maximum Temp. °F				Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	
PF22-1	J-1[2]	3/4	1000	300	34.4	–	–	40.5	–	3.13	–	No elevated temp. testing was conducted
PF22-2	J-1[2]	0	1000	300	–	–	–	34.1	–	2.79	–	No elevated temp. testing was conducted
PF23	J-1[2]	0	1000	900	16.5	–	–	–	–	–	–	Laminate blew apart due to excessive outgassing
PF24	NASA[2]	0	200	600	26.3	1.46	49.2	25.0	19.5	2.19	1.75	–
PF25	NASA[2]	5	200	600	–	–	–	–	–	–	–	No laminate was formed resin "washed out"
PF26	D1516-29Y[2]	4	200	600	18.3	1.52	58.6	32.9	24.7	3.14	2.65	–
PF27	D1516-29X[2]	3	200	600	20.5	1.54	53.6	33.8	26.4	3.12	2.74	–
PF28	D1516-29Z[2]	2-1/2	200	600	15.8	1.54	62.2	41.7	33.7	2.90	2.70	–
PF29	Narmco[2]	1/2	1000	600	13.6	1.58	–	33.0	24.0	3.09	3.09	–
PF30	Narmco[2]	1/3	1000	600	11.1	1.52	–	18.9	22.0	3.09	2.97	–
PF31	Narmco[2]	1/3	1000	600	16.7	1.56	–	34.7	26.0	3.22	3.00	–
PF32	Narmco[2]	1/3	1000	600	11.8	1.58	–	30.5	25.2	3.81	3.38	–
PF33	Narmco[2]	1/3	1000	600	15.5	1.52	63.8	36.1	24.9	3.70	3.13	–
PF34	D1516-30X[3]	1/3	1000	600	17.2	1.62	55.2	36.4	30.1	3.64	3.36	–
PF36	D1516-34R[2]	3-1/2	1000	600	4.2	–	–	–	–	–	–	Delaminated during trimming
PF38	D1516-33[4]	1/2	1000	600	21.8	1.51	53.2	44.4	29.7	3.13	2.81	–
PF39	D1516-31X[5]	1	1000	600	18.3	1.53	58.1	38.4	26.5	2.71	2.03	–
PF40	D1516-29X[2]	–	100	600	16.4	1.55	60.5	30.7	21.7	3.08	2.77	Laminate formed by vacuum bag technique

(1) All laminates were fabricated using Style 181 "E" glass cloth with an A-1100 finish
(2) PMDA-DAB resins in DMAC solvent
(3) PMDA-DAB resin in DMF solvent
(4) BTDA-DAB resin in DMAC solvent
(5) PMDA-DAB resin in NMP solvent

of resins and subsequent laminates were made with the PMDA-DAB system in DMAc. The initial work used a Hughes synthesized PMDA-DAB-DMAc resin designated J-1. Laminates PF-14 through PF-24 were formed with this resin system. Many conditions were attempted using this resin system. The pressures applied to the laminates were varied from 50 to 5000 psi with the best strength values obtained in the intermediate pressure ranges (i.e., 200 to 1000 psi). This indicated that with the resin systems in polar solvents, a moderate amount of pressure was necessary to achieve resin flow during the laminating operation. Pressure alone was not responsible for obtaining optimum strength because the laminating temperature was varied along with the pressure in many instances. In almost all cases the laminates cured at the higher temperatures achieved the best strengths.

There is a rule of thumb (with few exceptions), that those conditions of time, temperature, and pressure necessary to obtain laminates with optimum resin contents, densities, and low voids, also result in laminates with the highest flexural strengths and moduli.

To better illustrate the complexities in attempting to optimize the PMDA-DAB-DMAc system, the operations that were followed in the formation of the various laminates are discussed in the following sections.

Hughes J-1 Resin

Five laminates were formed at 500 psi pressure with the press temperature varied from 200 to 600°F at 100°F intervals. The five laminates were postcured for 2 hours at 600°F in air. The laminate with the best strength properties was PF-14-3 which was pressed at 400°F and postcured 2 hours at 600°F in air.

Two vacuum bagged laminates were formed at 50 psi pressure and at a maximum press temperature of 600°F. These vacuum bagged laminates had much higher strength properties than those formed at 500 psi pressure.

Three laminates were formed to determine the effect of variable pressures and temperatures on the properties of laminates formed with J-1 resin. The highest strengths were achieved at 750°F press temperatures while the effect of pressure was not clearly defined since both a 1000 psi laminate (PF-17) and a 5000 psi laminate (PF-18-9) showed comparable flexural strengths.

A laminate was vacuum bagged and cured at a maximum temperature of 350°F and pressure of 200 psi. This laminate could not be tested for strength properties due to delamination. This delamination was the result of presure build-up within the laminate, probably caused by vaporized solvent and/or condensation products.

A laminate was formed at a maximum temperature of 600°F and at a maximum pressure of 500 psi. Part of this laminate showed evidence of delamination; the other part had the highest flexural strength and modulus of any laminate made in the program to date. Laminate PF-21 was formed using CCA-1 carbon cloth as the reinforcement. This laminate was disappointing since the strength values were approximately half of those obtained on carbon cloth-phenolic laminates. The properties of those laminates discussed are summarized in Table I.

Laminates PF-22-1 and PF-22-2 were formed at 1000 psi pressure after being "bumped" five and two times, respectively, at low pressure. Both laminates were pressed at a 300°F maximum temperature with the resultant strength properties relatively high compared to previous laminates formed from J-1 resin. To improve the strength properties of the laminates formed from J-1 resin, another laminate was tried to introduce the layup to a heated press held at temperatures of 806, 850, and 900°F. This attempt at high temperature curing at a pressure of 1000 psi was unsuccessful with resultant poor interlaminar strength. The laminates were of such poor quality that they were not tested.

NASA-Langley PMDA-DAB-DMAc Resin

Two laminates were formed using submitted NASA resin which had been reduced to form a resin with 19.6 percent solids. One laminate

was formed at a pressure of 200 psi and the press temperature was raised in 50°F stages from 300 to 600°F over a 3-1/2-hour time period, held at 600°F for 4 hours and cooled in the press. This laminate did not exhibit any improved strength properties over previous laminates. The PMDA-DAB-DMAc resin used to prepare this laminate gelled when it stood for several days. The gel was mixed with additional DMAc to make up a gel-solvent mixture with the equivalent of 8 percent solids. This mixture was coated on the glass cloth and a laminate prepared from this material following the procedure used for PF-24. The resultant laminate was of such poor quality that all 12 plies could be manually separated. The laminate was not tested for strength properties. The physical properties of these two laminates are recorded in Table II.

Hughes PMDA-DAB-DMAc Resins

Three laminates were formed from Hughes synthesized PMDA-DAB-DMAc resins. The D1516-29X resin was synthesized in technical grade DMAc, the D1516-29Y resin was synthesized in dried reagent grade DMAc and the D1516-29Z resin was synthesized in DMAc at low concentration (2 percent). Examination of the flexural strength data presented in Table II indicates no significant difference between the resins made from technical DMAc or reagent grade DMAc. Laminate PF-28 showed somewhat improved flexural strengths over those strengths obtained from PF-26 and PF-27.

Narmco PMDA-DAB-DMAc Resin

Five laminates were formed using PMDA-DAB-DMAc resin synthesized by Narmco. These five laminates were prepared under identical time, temperature, and pressure conditions but the resin contents of the individual laminates were varied between 11.1 and 15.5 percent. The laminates formed from Narmco resin showed no improvement in strength properties over those formed using Hughes synthesized resins. The properties of this series of five laminates are tabulated in Table II.

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Hughes PMDA-DAB Resins in Various Solvents

Three laminates were formed using Hughes synthesized resins. The D1516-30X resin was synthesized in DMF, the D1516-34R resin in DMAc and the D1516-31X in NMP. All three laminates were formed at 1000 psi pressure and a maximum press temperature of 600°F. Laminates PF-34 and PF-39 exhibited almost identical flexural strength values of the same order of magnitude of previous DMAc resins. Laminate PF-36 experienced delamination during trimming and was not tested. The physical properties of these three laminates are recorded in Table II.

Vacuum Bag Layup

A vacuum bag layup was prepared according to the following procedure. The bagged layup was placed in a press under vacuum with 25 psi pressure for 21 hours with no heat. The temperature then was raised to 300°F over a 20-minute time interval and the pressure increased to 100 psi. The layup was held under these conditions for 1 hour and the temperature then increased to 350°F and held at this temperature for 2-1/2 hours. The bagged laminate was cooled and then placed in a 600°F press for 1 hour at 100 psi and removed hot. The flexural strength and modulus of this laminate were relatively high compared to the laminates previously formed at higher pressures. The physical properties of this laminate are recorded in Table II.

Hughes BTDA-DAB-DMAc Resin

A laminate was formed using a BTDA-DAB-DMAc resin synthesized at Hughes. This new anhydride resin system was investigated to determine if the low strength problems encountered were the result of the basic resin system as well as solvent-resin interaction. Laminate PF-38 was molded using the same 1000 psi pressure and 600°F maximum press temperature at which the latest PMDA-DAB-DMAc laminates were prepared. Examination of the physical properties

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recorded in Table II and subsequent comparison to PMDA-DAB-DMAc laminates formed under similar conditions, indicates the BTDA-DAB-DMAc resin system is conducive to the formation of laminates of higher strength than the laminates made from the PMDA-DAB-DMAc resin system.

3.4 ADDITIONAL STUDIES

A series of three moldings was prepared to determine the behavior of the precipitated J-1 powder under typical molding conditions. Two 3/4 inch diameter disks were compression molded at 300°F and 3000 psi for 1 hour. These moldings were dense and tough and showed very few voids and flaws. A 2-1/2 inch diameter disk was molded in the same manner as the previous two 3/4 inch disks and then subjected to postcuring from 275° to 600°F over a 66 hour time period. Prior to postcuring the disk had an excellent appearance and a density of 1.26 gm/cc; however, after postcure the specimen showed large blisters and voids indicating volatile emission and low vapor transmission of the material.

Five additional 2-1/2 inch diameter disks were molded from the polymer powder at 300°F and pressures varying between 3000 and 12,000 psi. Not all of these moldings were postcured. The best appearing disks were those molded at the higher pressures with no postcuring. Their density varied between 1.34 and 1.39 gm/cc.

Coating and adhesion studies were carried out with unpigmented J-1 resin in DMAc. All studies were conducted using a 20 percent (by weight) solids content resin. Various cleaning and curing procedures were investigated for both stainless steel and aluminum substrates, and the adhesion of the coatings on stainless steel was determined.

Forty type 302 stainless steel test coupons (1 x 4 x 0.005 inches) were dip-coated in the 20 percent J-1 resin and air dried at room temperature for periods of 1 to 7 days prior to cure. Surface cleaning and coating cure were the processing variables investigated in this test series. The test coupon surfaces were prepared by both alkaline

degreasing methods and depassivation procedures, and both thermal and ionizing radiation techniques were used to cure the coatings. The most flexible and best adhering coatings were obtained on the electrochemically depassivated substrates which had thermally cured coatings.

Additional coating studies were conducted on both 2024 aluminum alloy and 17-7 PH stainless steel. The aluminum alloy surfaces were prepared by liquid honing, chromic acid immersion and anodic etching in hot alkali. The stainless steel alloy surfaces were prepared by liquid honing, alkaline cleaning and anodic etching in concentrated sulfuric acid. The application of resin was limited to dip coating with air-drying of each coating prior to recoating. The coatings were cured at either 350° or 400°F in air or by gamma irradiation from a Co^{60} source.

The results of these studies indicated that the surface preparations did not result in the full potential for chemical bond between polymer and substrate to be realized, even where adhesion to the substrates was considered acceptable. These tests further indicated that proper solvent removal and curing may yield acceptable coating film flexibility.

Two pairs of test specimens were prepared for 180-degree peel testing. In one cast two type 302 stainless steel members, one 1 x 4 x 0.050 inch the other 1 x 4 x 0.005 inch, were detergent cleaned and anodically treated in HCl. The resin was brush coated on one side of each member and a layer of glass beads spread on the 0.050 inch thick piece. The two coated surfaces were mated and oven-cured for 2 hours at 400°F. Two such specimens showed no appreciable adhesion or bond line integrity.

A second pair of specimens was prepared from 0.005-inch type 302 stainless steel sheet cleaned in the same manner but dip-coated and air-dried until still tacky. Mating pairs were joined and vacuum dried for approximately 24 hours. One specimen was thermally cured at 400°F for 2 hours and the other cured with gamma radiation in a Co^{60} source. These specimens showed a neglible adhesion of 0.3 pound/inch width at a peel rate of 1 inch per minute.

A 1/8 inch thick sample of fiberglass reinforced Pyrrone laminate was obtained from NASA-Langley Research Center for X-band dielectric measurements. Three disk specimens of 2.135 inch diameter were evaluated in a resonant cavity dielectrometer at 9.28 GHz at 25°C and one specimen also at 225°C. The results of these tests are presented in Table III.

Table III. Dielectric Properties of Pyrrone Laminates

Specimen	Thickness, inch	Wavelength Per Specimen	Temper- ature, °C	Relative Permittivity	Loss Tangent
A	0.125	0.1965	25	4.514	0.0463
A + B	0.250	0.3856	25	4.364	0.0365
A + B + C	0.375	0.5757	25	4.328	0.0358
A	0.125	0.1936	225	4.396	0.0098
A	0.125	0.1071	25	4.536	0.0376

The high loss value at room temperature might have been due to absorbed water. After the specimens shown on Table III were dried for 24 hours in a 125°C oven and allowed to cool down in a desiccator, the following results were obtained:

A	0.125	0.1890	25	4.213	0.0085
B	0.125	0.1897	25	4.242	0.0083

Thus, it would appear from these preliminary measurements that the subject material is moisture sensitive.

The high temperature (225°C) value reported above is not corrected for the thermal expansion of the specimen. The expansion coefficient of the material is unknown, but if is assumed to have a value of 1×10^{-5} inch per degree C the thickness increase for specimen A at 225°C is 0.00025 inch. The "corrected" values of relative permittivity and loss tangent now become 4.38 and 0.0098, respectively.

3.5 CONCLUSIONS

The flexural strengths of laminates formed from resins synthesized in DMAc, DMF, and NMP were lower than anticipated. Three factors probably affected the results. First, the solvent-free or nearly solvent-free resin had very poor flow characteristics. Therefore, it was necessary to leave solvent in the resin in order to provide sufficient flow for processing. Removal of the solvent during the later stages of cure and during postcure consequently left a high void content. Second, the solvent remained tightly bound to the polymer even at high temperatures. Third, at high temperatures the solvent probably reacted chemically with the polymer and possibly interferred with the curing reactions.

The poor flow characteristics were the most important of these factors. In Pyrrones, as in other polymers, weaknesses in the gross structure of the cured polymer exist along boundaries that separate two regions where inadequate flow occurred prior to cure. These gross structural weaknesses can eclipse completely the strengths or weaknesses inherent in the fundamental chemical structure of the polymer.

The poor flow characteristics of the resin stemmed from the infusibility of the solvent-free polymer. A possible chemical reason for this infusibility lies in the ionic nature of the A-A-A polymer, which can be represented by the zwitterionic structure XVII.
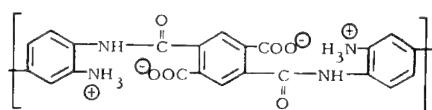
XVII

Ionic crosslinking enhances the crystallinity of the polymer and makes it high melting. Conversion of the A-A-A polymer to the polyimide (II) or the polybenzimidazole (III) reduces the ionic character of the polymer, but this offers no improvement in flow properties since the condensed aromatic nuclei formed in the conversion also render the polymer infusible.

A solution to the problem of increasing flow was to reduce the ionic character of the A-A-A polymer. This approach led to the work discussed in Phase II of this program.

The second problem, the tenacity of the solvent, is also the result of the strongly polar nature of the polymer. Because of the polar nature, a strongly polar solvent had to be employed as the synthesis medium. Strong attractions between the polymer and the solvent were inevitable. DMAc, the first choice of solvent, is known to form stable complexes with a variety of organic and inorganic materials with considerable ionic character. For example, DMAc forms a crystalline complex with dicarboxylic acids, the complex containing two moles of DMAc for each mole of acid (ref. 11). It is not surprising, therefore, to expect that polar solvents would be held tenaciously by the Pyrrone polymers. Eventually, this solvent is removed during postcure and leaves voids that diminish the strength of the cured product.

Fortunately, the solution for the second problem is related to that of the first. Reducing the ionic character of the polymer will permit less polar solvents to be employed. The combination of a less polar polymer and a less polar solvent should minimize the tendency to bind the solvent to the polymer.

The third problem, the stability of the amide solvents at high temperatures, also is peculiar to the amide solvents and could be eliminated with the solvent. The odor of acetic acid detected around the curing polymer was not noticed when purified DMAc was used. Consequently this odor is not necessarily an indication that the solvent had hydrolyzed. However, hydrolysis may still exist as a possible problem, since both the acid and the amine products may remain bound to or reacted with the polymer, as discussed in Section 2.0. While hydrolysis of DMAc is extremely slow at room temperature, the rate is appreciable at the elevated temperatures required for cure. Further study of these effects was obviated by the approach pursued in Phase II.

During the lamination study it became apparent that flexural strengths on the order of 40,000 psi and moduli of approximately

3 million psi were maximum values for the PMDA-DAB resins in polar solvents. Variation of laminating temperatures and pressures indicated that the best flexural strength values were obtained for intermediate pressure (200 to 1000 psi) and temperatures of 600-750°F.

The laminate formed using a BTDA-DAB-DMAc resin exhibited a higher room temperature flexural strength than any of the PMDA-DAB-DMAc laminates prepared in Phase I. This was accomplished with the first laminate tried which used no special techniques. The problem of low strengths encountered with the PMDA-DAB laminates was not entirely due to polymer-solvent interaction to form a polyelectrolyte, or to hydrolytic breakdown of solvent during the polycondensation, but was due to the anhydride selected for the polymer system.

Throughout the laminating program of Phase I an acidic odor of unknown volatile materials emanated from the curing laminates. This odor was not that of the parent solvent; thus, it was concluded that the solvent was modified in some manner (probably hydrolysis as a result of reaction with water of condensation) with subsequent oxidation. Attempts to reduce the amount of solvent present in the curing resin met with failure. To maintain the necessary degree of flow to successfully form a laminate, a substantial amount of solvent had to remain in the resin. The resin in its present form had unsatisfactory flow, and degradation due to unfavorable behavior of the solvents appeared to be inherent in the resin system. The Phase II study shows that these assumptions were verified when successful laminates were formed by synthesizing resins that achieved their flow by bonding the solvent internally.

4.0 PHASE II − POLYMERS FROM ETHYLENE GLYCOL ESTERS

The evaluation of the materials produced in Phase II of this program is based upon the chemical behavior (Section 4.1), character- ization of the resins (Section 4.2), the physical properties of laminates (Section 4.3), the thermal and electrical properties of the laminates (Sections 4.4 and 4.5) and additional studies on moldings, foams and filament wound composites (Section 4.6). The conclusions drawn from the Phase II investigation are presented in Section 4.7.

4.1 POLYMER SYNTHESIS

The first syntheses of BTDA-DAB resins in ethylene glycol (EG) followed the procedure previously employed at NASA-Langley Research Center. A slurry of BTDA in EG was warmed until the BTDA dis- solved, and the solution was added to an EG solution of an equal molar quantity of DAB. All operations were performed in apparatus purged with argon, as shown in Figure 3.
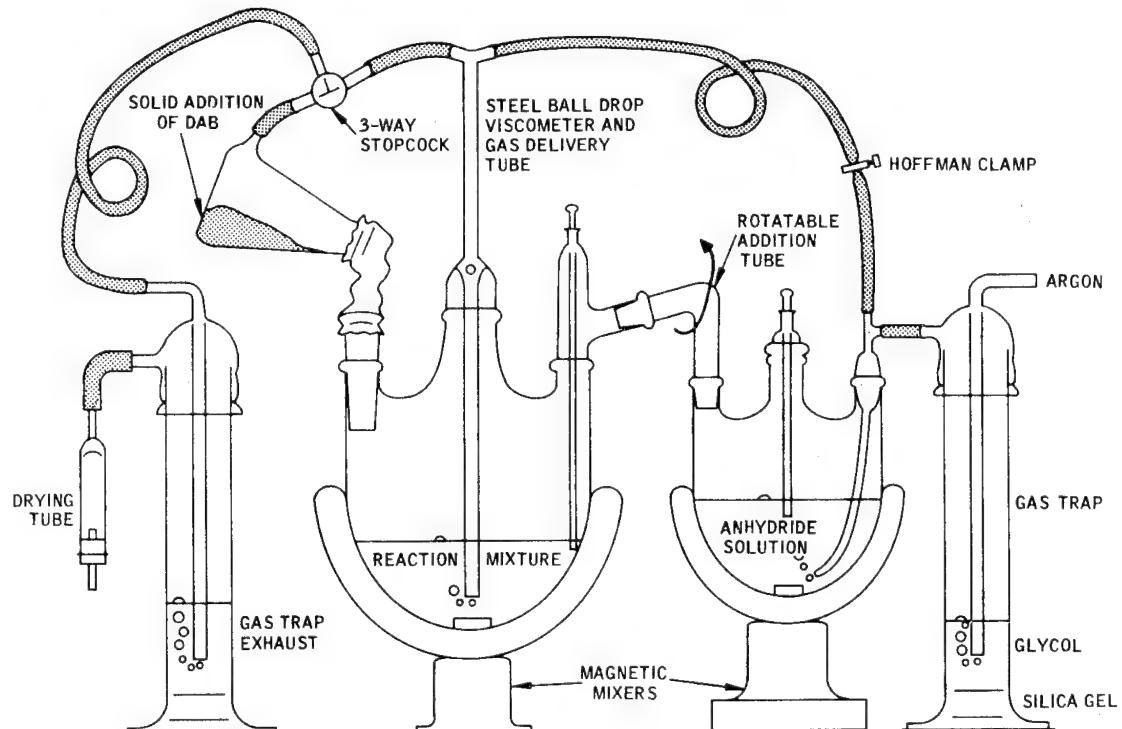
Figure 3. Apparatus for Resin Preparation

Resins Synthesized at Low Solids Content

The reactions were carried out at 75°C, slightly higher than the 60 to 70°C temperatures previously used. Concentrations of reactants used were calculated to give a solution with about 13 percent solids; the resulting solution was concentrated in a rotary evaporator to a solids content of 25 to 30 percent. Experimental details for a specific preparation are as follows.

A 192.6 gm (0.9 mole) quantity of DAB was added to 1500 ml of purified ethylene glycol at a temperature of 120°C under argon. A solution of BTDA (prepared by dissolving 289.6 gm (0.9 mole) of BTDA in 1500 ml of purified EG at 120°C) was added to the DAB solution in the reaction vessel, and the mixture was stirred at 70-75°C for 10 minutes. Three batches prepared in this manner were combined and the resultant batch of resin was concentrated to 1 gallon in the Rota-film evaporator at a temperature of 70-75°C.

A falling ball viscometer was used to follow the progress of this type of reaction. Viscosity data were not expected to be precise because the temperature of the reaction mixture could not be precisely controlled. In the first experiments, therefore, the viscometer tube was not jacketed to control the temperature. Because of its high specific heat, however, the EG solution changed temperature very slowly.

Although the DAB solution was already dark in color, the solution turned considerably darker within the first 10 minutes after the BTDA solution was added. An approximately 0.3 molar solution of monomers produced a yellowish flocculent precipitate after 410 minutes at about 75°C. During this time the viscosity of the solution increased from 25 to 81 centipoises. No sudden changes in viscosity or appearance occurred. Prolonged heating merely caused the precipitation of additional material. The polymer so derived was a "brick dust" type of material that was insoluble in all solvents used but concentrated sulfuric acid. Although it failed to melt on a melting point block, it underwent sufficient flow in a press to allow a part to be molded.

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When a similar reaction was carried out at 100°C, polymer precipitated only 28 minutes after mixing. No appreciable increase in viscosity could be detected prior to precipitation, however. Lower temperatures were definitely more desirable for controlling the extent of reaction.

Resins Synthesized at Higher Solids Content

Evaporation of solvent in the rotary evaporator not only was a time-consuming process, but it also advanced the resin to an undetermined extent. Bath temperatures of 70 to 75°C were required, although the temperature of the evaporating solution actually may have been considerably lower. It was found that more concentrated resins could be prepared directly from more concentrated solutions of the monomers. Most of the subsequent solutions were prepared in such a manner that the weight of BTDA and DAB used equaled about 23 percent of the weight of the final solution. This concentration, that will hereafter be called a 23 percent solids concentration, was found to be quite satisfactory for coating the reinforcing fabric. Experimental details for a typical preparation of this type follow.

A solution of BTDA composed of 193.2 gm (0.6 mole) in 300 ml of EG at 76°C was mixed with a DAB solution composed of 128.4 gm (0.6 mole) in 735 ml of EG at 75°C. The temperature rose to 78°C on mixing, and after about 10 minutes the resultant resin was cooled and stored under argon.

A temperature of 75°C or greater was necessary to retain the DAB in solution at the concentration required for preparation of a 23 percent solids resin. At this temperature and concentration the polymer began to precipitate after about 320 minutes. At this point the polymer was more soluble in the reaction mixture than it was in EG; consequently, the polymer that precipitated from the concentrated solution may have been more advanced than that first precipitated from a more dilute solution.

The precipitate from the 23 percent solids resin was separated and washed in methanol. This polymer, which had not undergone

prolonged heating after precipitation, was fusible and soluble in such solvents as DMAc, DMSO, and cold dilute aqueous potassium hydroxide.

The viscosities of the more concentrated reaction mixtures were determined with a falling ball viscometer that had been jacketed and surrounded with the bath fluid to maintain better control of the temperature. As the reaction progressed, the viscosity at 75°C increased from an initial value of 26 centipoises to about 50 centipoises at the point of precipitation.

Preparation of BTDA-EG Esters

In carrying out these syntheses it was observed that BTDA was not soluble in EG at room temperature, but that once the mixture was heated to dissolve the BTDA nothing precipitated on cooling to room temperature. Obviously the dissolution process involved an esterification reaction like that shown by the equation below.
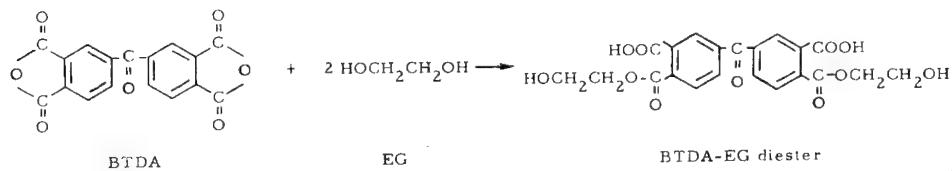
Complete esterification would require more strenuous conditions than those employed (warming at 80 to 120°C).

The anticipated course of reaction between the BTDA-EG diester and DAB is indicated below.

VIII

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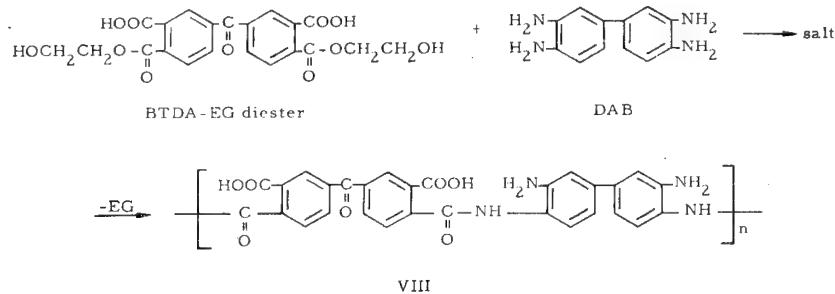
Thus the initial product of the reaction would be a salt of the monomers. Condensation to form a polymer from the salt would be anticipated to lead to the A-A-A polymer (VIII) or its zwitterionic form (XI). The alternative reaction, in which water would be eliminated and the polymeric product would retain the ester groups, is considered much less probable since aminolyses of esters ordinarily occur far more readily than aminolyses of carboxylic acids. If the A-A-A polymer was indeed the product, the basic structure of the polymer was unchanged from that secured from the anhydride and DAB in DMAc. The differences in behavior probably were due to differences in molecular weight and in end groups. When the anhydrides and DAB are reacted directly in polar solvents, the extreme reactivity of the anhydrides with the amine probably produced a high degree of polymerization with the resultant polymer having a high molecular weight. The esters, however, being less reactive, produced polymers with lower degrees of polymerization which could be terminated at relatively low molecular weights by precipitation from ethylene glycol.

In view of the probable course of reaction, it was considered desirable to convert BTDA (or the BTDA-EG diester) to the tetraester prior to reaction with DAB. This conversion was carried out both with and without an acid catalyst.

$$
\text{BTDA} + 4\ HOCH_2CH_2OH \xrightarrow[\substack{\text{or}\\\text{heat to}\\200°C.}]{\substack{CH_3C_6H_4SO_3H\\\text{at }80°C,}} \text{BTDA-EG tetraester} + 2\ H_2O
$$

BTDA-EG tetraester

+ 2 H₂O
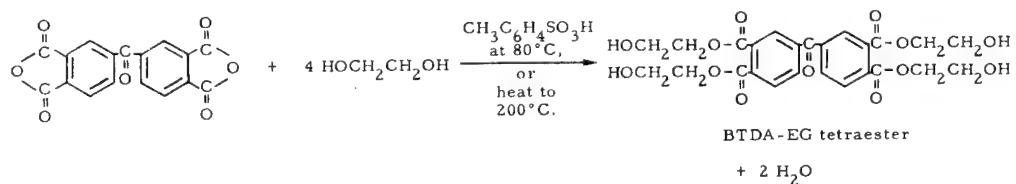
The acid-catalyzed esterifications were conducted at the boiling point of a glycol-benzene mixture in the presence of p-toluenesulfonic acid as a catalyst. Water was removed as the benzene azeotrope. The uncatalyzed esterifications were accomplished at the boiling point of the glycol solution; the water was removed continuously by distillation. Both methods produced considerably more than the theoretical amount of water and the quantity of water produced, therefore, served only as

a vague indication of the completeness of reaction. Possible sources of water other than the esterification are indicated by the following equations:

$$2 HOCH_2CH_2OH \xrightarrow{H+} HOCH_2CH_2OCH_2CH_2OH + H_2O$$

$$HOCH_2CH_2OCH_2CH_2OH \xrightarrow{H+} \begin{array}{c} H_2C \overset{O}{\diagup} CH_2 \\ H_2C \underset{O}{\diagdown} CH_2 \end{array} + H_2O$$

$$HOCH_2CH_2OH \xrightarrow[\text{or H+}]{\text{heat}} CH_3CHO + H_2O$$
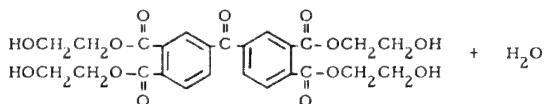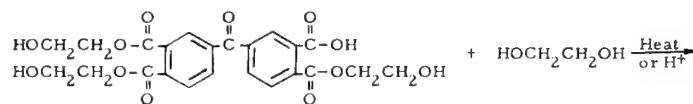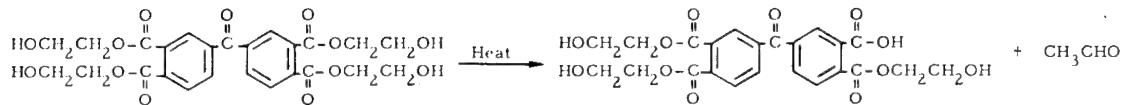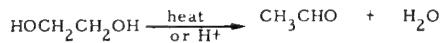
Water-producing side reactions interfered most in the acid-catalyzed reaction; consequently, the uncatalyzed reaction seemed preferable. Since the product of the acid-catalyzed reaction was noticeably more viscous, the telomerization of glycol is assumed to be the primary side reaction. Water derived from the uncatalyzed ester-ification had the distinctive odor of acetaldehyde; however, a semi-carbazone prepared from the aqueous distillate was not the acetaldehyde derivative. The ester was used in the solution in which it was prepared without purification. Several typical ester preparations are described as follows.

A 96.6 gm (0.3 mole) quantity of BTDA and 1.0 gm of p-toluenesulfonic acid monohydrate were dissolved in 150 ml of hot EG. The solution was cooled to below 80°C, 200 ml of benzene were

added and the mixture was refluxed for 48 hours under an azeotropic trap. From this reaction, 17 ml of lower phase were collected in the distillate, and a refractive index indicated it was practically 100 percent water. (Theoretical water of reaction was 10.8 ml.) The benzene was distilled from the mixture to leave the ester solution, which was an extremely viscous liquid with very little tendency to flow.

Another ester was prepared by adding 96.6 gm (0.3 mole) of BTDA to 530 ml (585.1 gm) of purified EG which had been heated to 110-130°C. The reaction mixture began boiling at 180°C with further heating. As the water which formed was distilled from the mixture, the temperature of the boiling mixture rose to 199°C. During the distillation the temperature at the top of the distillation column never rose above 178°C. The total aqueous distillate weighed 28.17 gm, had a light yellow color, possessed an odor reminiscent of acetaldehyde and had a refractive index (sodium D at 25°C) of 1.3547 which corresponds to a composition of 22 volume percent glycol - 78 volume percent water. An additional 24.4 gm of solvent with a refractive index of 1.4284 (corresponding to a 97 percent glycol - 3 percent water composition) were distilled off leaving an ester solution weighing 627.6 grams. A Karl Fischer titration of the two fractions of distillate indicated they contained 85.1 percent and 3.9 percent water. Thus the Karl Fischer method showed that the total yield of water was 24.9 gm, whereas the estimate based on the refractive indices was 22.7 gm. Theoretically the yield should have been 10.8 gm for the esterification.

Since the ester has not yet been characterized (although it has been determined that it can be isolated as a solid), and since side reactions are clearly occurring during the esterification, it still is not known that the product is actually tetrakis(2-hydroxyethyl) 3,3',4,4'-benzophenonetetracarboxylate. It seems safe to assume, however, that it is a more completely esterified product than that obtained by simply dissolving the dianhydride in EG. Whatever the actual structure is, it will be referred to as the BTDA-EG tetraester.

The BTDA-EG tetraester probably contains a small amount of low molecular weight polyester, although polyester formation was suppressed

by using a huge excess of ethylene glycol. When the preferred procedure was used, even at the end of the esterification the molar ratio of glycol to ester was 26:1 and the ratio of equivalents of hydroxyl groups on the ester to equivalents of hydroxyl groups on the glycol was 13:1. BTDA-EG polyester should be cleaved by DAB to give the same products as those formed from the simple tetraester.

The first preparation of the tetraester is believed to have been incomplete. A reaction of this product with DAB for 5 hours at 75°C produced a polymer which was insoluble in the cold resin but soluble in the warm resin at a concentration of about 30 percent solids. Condensation of a more completely esterified product with DAB gave no precipitate after 4 days at 100°C. In both cases there was little change in viscosity during the reaction, but the solution became darker in color. A 5 percent excess of BTDA-EG tetraester did not change this behavior. Obviously the use of the BTDA-EG tetraester instead of the diester caused a considerable change in the nature of the reaction products.

Heating the reaction mixture containing DAB and the BTDA-EG tetraester at reflux for about 1-1/2 to 3 hours (depending on the prior treatment) formed a resin that became extremely viscous on cooling or even gelled at the reaction temperature. The formation of a thick, gummy paste or gel-like product, rather than a granular precipitate such as that obtained from DAB and the BTDA-EG diester, was a noteworthy feature of these preparations. This behavior was consistent with diminished ionic character and a lower degree of crystallinity.

The progress of the polymerization was followed by making relative measurements of the viscosity of the solution. The column of liquid in the falling ball viscometer was not maintained at a constant temperature; but by making measurements in the same manner each time, adequate relative values could be obtained in spite of gradual cooling of the solution. The viscosity increased from less than 10 centipoises to about 30 centipoises at the time of gelation.

Resins Synthesized from BTDA-EG Esters

A series of resins was prepared from DAB and BTDA-EG tetraester. The solid DAB was dissolved in the EG solution of the tetraester

at about $100^{o}C$, and the resulting solution was then heated to reflux as illustrated by the following typical resin preparation.

A 615. 8 gm quantity of 0. 3 mole BTDA-EG tetraester solution was heated to $100^{o}C$ under argon and 64. 2 gm (0. 3 mole) solid DAB was added. The mixture was stirred and heated to reflux. Periodic viscosity readings were taken at the reflux temperature. After 2 hours the viscosity had increased from 5. 0 to 13. 5 centipoises. The mixture was cooled rapidly in an ice bath, and the resultant resin was stored under argon. The cooled resin was an extremely viscous, non-pourable resin.

A plot of viscosity against reflux time indicated that the results were not readily reproducible, probably because of variations in the time required to reach the reflux temperature. Viscosity readings appeared to be a more reliable method than reflux time for monitoring the extent of resin advancement. From this study it was concluded that at a 23 percent solids concentration, the viscosity of the refluxing reaction mixture should not greatly exceed 7. 6 centipoises if a resin of workable fluidity at room temperature is desired.

A better correlation between reaction time and viscosity could be obtained by adding the solid DAB to the refluxing BTDA-EG tetraester solution. An unexpected result, however, was that the viscosity increased much more rapidly than it did when the initial addition of DAB was made at $100^{o}C$, and the solution was subsequently heated to reflux temperature. For example, when the initial addition of DAB was made at $100^{o}C$ and the reaction mixture was subsequently heated at reflux for 2 hours, the viscosity was the same as that of a similar reaction mixture obtained by adding the DAB to the ester at the reflux temperature and heating the mixture at reflux for only 30 minutes. Furthermore, the products of the latter type of preparation were more fluid at room temperature. Possibly the reactions initiated at the boiling point are different from those which occur when the reactions are initiated at lower temperatures. This could be a consequence of competitive reactions with different activation energies.

The viscosities of the reaction mixtures increased gradually and smoothly at the reflux temperatures. When the mixtures were cooled

to room temperature those mixtures that had a viscosity of less than 10 centipoises, at the reflux temperature, remained fluid. However, those mixtures that had a viscosity greater than 10 centipoises, at the reflux temperature, became extremely viscous.

This behavior is best illustrated by a series of four resins prepared in the following manner. All four resins were prepared by adding 64.2 gm (0.3 mole) of solid DAB to 610.8 gm (0.3 mole) portions of the ester solution while the ester was being stirred at gentle reflux under argon. Viscosity measurements were made periodically at the reflux temperature. After the reactions had proceeded to the desired degree of advancement, as determined by the viscosities, the mixtures were cooled in ice and stored under argon. The viscosities at the reflux temperature and the appearance of each at room temperature are presented in Table IV.

Resins were prepared also from PMDA and DAB using essentially the same procedures that were developed for the BTDA-DAB

Table IV. Viscosity Properties of a Series of BTDA-DAB-EG Resins

Run D1516-59		Run D1516-60		Run D1516-62		Run D1516-61	
Viscosity, centipoises	Reaction Time, minutes	Viscosity, centipoises	Reaction Time, minutes	Viscosity, centipoises	Reaction Time, minutes	Viscosity, centipoises	Reaction Time, minutes
6.5	8	6.5	8	5.5	7	5.5	8
7.5	20	7.0	16	7.0	24	8.0	34
7.5	25	7.5	25	8.0	44	9.0	44
		8.5	35	10.0	69	10.0	59
		9.5	43	11.0	89	11.0	74
						12.0	84
						13.5	94
Easily pourable		Slightly less pourable than D1516-59		Barely pourable		Still pourable but even less so than D1516-62	

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resins; however the PMDA-EG esters were used in these preparations. A typical PMDA-DAB-EG resin synthesis is illustrated by the following preparation.

The PMDA-EG ester was prepared by adding 130.8 gm (0.6 mole) PMDA to 900 ml ethylene glycol and heating the mixture to gentle reflux. The water of reaction was removed during the reaction by distilling off a water-glycol mixture. The reaction was continued overnight, but the heating rate was such that only 10 ml of the water-glycol distillate was collected during the overnight reaction time. The reaction was run for an additional eight hours at a faster heating rate bringing the total volume of distillate for the reaction to 200 ml. This volume of distillate contained 55 ml of water as determined by periodic refractive index checks. The distillation began at a head temperature of approximately 160°C with the temperature of the reaction mixture at approximately 190°C. The total reaction time was approximately 30 hours with the total yield of ester solution being 933.1 gm.

The resin was prepared by adding 64.2 gm (0.3 mole) of solid DAB to 466.5 gm of ester solution containing 0.3 mole of the PMDA-EG ester which had been heated to 140°C. The reaction mixture was heated to approximately 190°C in 40 minutes and was refluxed at this temperature for 45 minutes until the mixture had a viscosity (at 190°C) of approximately 7.5 centipoises (as determined by the falling steel ball viscometer). The resultant resin was cooled to room temperature and stored under argon.

Preparation of Scaled Up Batches of Resins

Initial preparation of smaller scale batches and the laminates subsequently formed from these resins demonstrated that high strength laminates could be formed from resins synthesized from the BTDA and PMDA tetraesters. Resin batches up to this point had been prepared in 0.3 to 0.9 mole batches which represented volumes of approximately 1/2 to 1-1/2 quart. At this time it was decided to scale up the size of the resin batches to determine whether resins with consistent properties could be prepared by the same techniques used for the smaller

batches. A typical large scale BTDA-EG tetraester synthesis and preparation of resin from the large batch of tetraester is illustrated by the following preparation.

The BTDA-EG tetraester was prepared by adding 966.7 gm (3.0 moles) of BTDA to 4000 ml of hot ethylene glycol, heating the mixture to gentle reflux and reacting for 60 hours. The water of reaction was continuously removed through a heated Vigreaux column. A total of 320 ml water-glycol mixture was distilled from the reaction mixture. Based upon a refractive index of 1.3586, this corresponds to a total of 238 ml of water or 79 ml water per mole of ester. The ester was diluted with 760 ml fresh ethylene glycol to bring the concentration of the final resin to approximately 25 percent solids by weight. The ester solution was divided into two 1.5 molar portions weighing 2897 gm each.

The resin was prepared by adding 321.2 gm (1.5 mole) solid DAB to 1.5 mole of the refluxing ester solution under argon. The reaction was continued at reflux for 130 minutes to bring the viscosity at reflux to 8.5 centipoises. The resin was cooled in an ice bath and stored under argon.

After several scaled up batches of the type illustrated by this synthesis had been run, it became apparent that variations in viscosity of resins at room temperature were occurring which caused trouble in consistent impregnation of the reinforcement fabric for laminates.

These variations were assumed to be due to errors in reflux temperature ball-drop viscosity readings taken during synthesis. Since the end point of this reaction depends entirely on the ball-drop viscosity, and the temperature of the reaction mixture greatly affects the viscosity, it was thought that a vapor heated jacket around the ball-drop column would improve the precision of the viscometer. Thus, two designs were tried, (Figure 4,) and it was found that design No. 2 permitted higher precision among sets of readings.

The flask of ester was heated to reflux, and when reaction mixture and column reached temperature equilibrium, viscosity readings were taken every 15 minutes over a 5-hour period. This experiment

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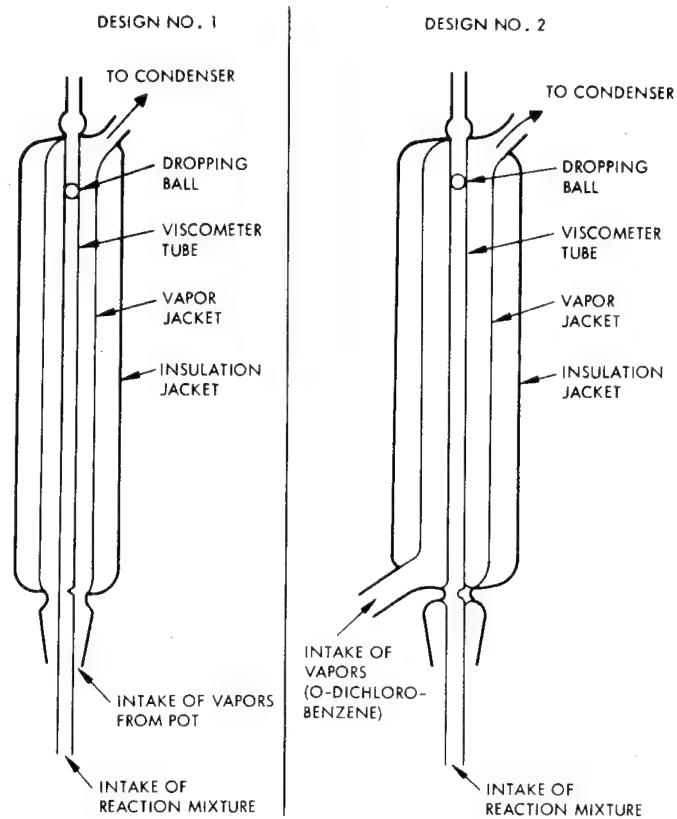
Figure 4. Design Variations for Vapor
Heated Ball-Drop Viscometer

showed that readings did not vary more than 0.2 centipoises over the
total of 60 determinations. However, in the first 0.3 molar experi-
mental run it was found that after DAB addition, no temperature
equilibrium could be obtained between reaction mixture and viscometer
column in Design No. 1. On examination of condensates from the
vapor column, a definite amine odor could be detected. Evidently some
side reaction or DAB decomposition occurs which depresses the vapor
temperature. When viscometer Design No. 2 was tried, ethylene gly-
col vapor was used first to heat the column; but viscosity readings
were extremely difficult to make because a few minutes after the
reaction mixture was drawn into the viscometer, it would begin to boil.
Obviously, readings had to be made before this occurred. Finally,
o-dichlorobenzene vapor (B. P. = 181°C) was used to heat the viscom-
eter column (Design No. 2), and the reaction mixture temperature was
kept at approximately 180°C. This method was found to be entirely

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satisfactory. The second viscometer (Design No. 2) was merely a modification of Design No. 1 and no re-calibration was necessary.

After the reliability of this modified viscometer had been verified, several 0.6 molar batches of resin were run to establish the optimum viscosity necessary for reinforcement impregnation and laminate processing. A series of three batches were run by heating 1079.0 gm (0.6 mole) of the tetraester to reflux under argon, adding 128.4 gm (0.6 mole) of solid DAB and reacting to various end point viscosities. A fourth batch was prepared under the same conditions only at 1.5 molar concentrations of tetraester and DAB. This series of resin preparations established that an end point viscosity of 3.0-3.6 centipoises was regarded as optimum for glass cloth impregnation and laminate processing. End point data for this series of resins is given in Table V. All end point viscosities were observed at 180°C.

Once the end point viscosity necessary to produce the desired processing properties had been established, the resin scale up was continued. Three batches of BTDA-DAB-EG resin were synthesized by heating 2732.5 gm (1.5 mole) of BTDA-EG esters to reflux under argon and adding 321.0 gm (1.5 mole) of DAB. These reaction mixtures were heated to end point viscosities in the 3.0-3.1 centipoise range, cooled in an ice bath and stored under argon. These three batches then were blended together with the D1516-81D batch from the prior end point viscosity study to make up a master batch of resin

Table V. End Point Viscosities for BTDA-DAB-EG Resins

Batch	End Point Viscosity, Centipoises	Reaction Time, Minutes	Remarks
D1516-81A	2.5	45	0.6 molar
D1516-81B	3.0	95	0.6 molar
D1516-81C	3.6	145	0.6 molar - regarded optimum for impregnation
D1516-81D	3.3	130	1.5 molar

which was designated BED-1. The volume of these four batches, when blended was approximately 3 gallons. This BED-1 master batch was put up in polyethylene bottles and stored at 40°F for further evaluation as a laminating resin.

A small batch of PMDA-DAB-EG type resin was synthesized using the same apparatus and techniques established for production of the BTDA-DAB-EG resins. The PMDA-EG ester was prepared by the addition of 872.4 gm (4.0 mole) of PMDA to 4000 ml of hot ethylene glycol. The mixture was heated to gentle reflux under argon, and water of reaction removed by distillation of water-glycol mixtures through a heated Vigreaux column. The reaction mixture was refluxed for 100 hours and 525 ml of water were collected (131 ml water/mole PMDA). A 2170 ml quantity of fresh ethylene glycol was added to the ester solution to bring the final weight of solution to 6147.7 gm.

The PMDA-DAB-EG resin was prepared by adding 192.9 gm (0.9 mole) of solid DAB to 1383.3 gm (0.9 mole) of the gently refluxing PMDA-EG ester under argon. The reaction temperature was brought to 180°C and its course followed by taking periodic viscosity readings of the reaction mixture using the vapor-heated ball drop viscometer. The reaction was discontinued when a viscosity of 3.4 centipoises (taken at 180°C) was reached after a reaction time of 80 minutes. The resin was cooled in an ice bath and stored under argon for evaluation as a laminating resin.

Preparation of Standard Resin Batch BED-2

Processing studies conducted with the BED-1 resin indicated that the current techniques for resin production were conducive to the formation of high strength laminates. Thus, it was decided to produce a large batch of BTDA-DAB-EG type resin for further processing studies and physical property evaluation.

A large batch of the BTDA-EG tetraester was produced by adding 2416.8 gm (7.5 mole) of BTDA to 10 liters of hot ethylene glycol with stirring at reflux for 72 hours. The water of reaction was removed

by continuous distillation through a heated Vigreaux column. A total of 1330 ml of water-glycol mixture was collected. This water-glycol mixture had a theoretical water content of 672 ml (89 ml/mole). A 1500 ml quantity of fresh ethylene glycol was added to the product so that the eventual resin produced by reaction with DAB would be at a solids content of approximately 25 percent. The net weight of the ester solution was 13,660.5 gm (1821.4 gm/mole).

Five 1.5 molar batches of BTDA-DAB-EG resin were synthesized from this tetraester by adding 321.0 gm (1.5 mole) of solid DAB to 2732.1 gm (1.5 mole) of BTDA-EG ester at reflux under argon. The reaction mixtures were refluxed to the desired end point viscosities, cooled in an ice bath and stored under argon. The reaction data for the five individual batches are recorded in Table VI.

A 7.5 molar master batch of BTDA-DAB-EG resin was prepared by mixing the five 1.5 molar batches at room temperature with stirring. The volume of this large batch was approximately 3-1/2 gallons. This large batch was considered to be the standard BTDA-DAB-EG type resin to be used for evaluation of mechanical, thermal and electrical properties of the laminates throughout the remainder of the program. This standard resin was designated BED-2 and was stored under argon at room temperature.

Table VI. Reaction Data for Five 1.5 Molar
BTDA-DAB-EG Resin Batches

Batch	Reaction Time, Minutes	End Point Viscosity, Centipoises
D1516-93A	120	3.3
D1516-93B	140	3.4
D1516-93C	145	3.2
D1516-93D	145	3.3
D1516-93E	145	3.3

4.2 POLYMER CHARACTERIZATION

During Phase II, it became apparent that synthesizing the resins
in ethylene glycol resulted in the formation of laminates of greater
strength. The criteria selected for evaluation of the resins were,
again, the flexural strength and modulus of the laminates.

Molecular Characterization

The molecular structures of three initial BTDA-DAB-EG resins
were characterized by elemental analysis. The first two were made
from what is assumed to be BTDA-EG diester diacid and the third
from the BTDA-EG tetraester. In general, solvents such as chloro-
form, trichlorobenzene, acetone, dioxane and methanol are very poor
solvents for these polymers, while the more polar solvents such as
DMSO, DMAc and DMF are more effective. EG lies between these two
groups in its ability to dissolve the polymeric products.

When the BTDA-EG diester is reacted with DAB, the first pro-
duct formed is a salt of the tetraamine and the dicarboxylic acid:

$$H_2N-\!\!\!\!\bigcirc\!\!\!\!\overset{NH_2}{\underset{NH_3^{\oplus}}{\bigcirc}}\quad \overset{\ominus}{OOC}-\!\!\!\!\bigcirc\!\!\!\!\overset{O}{\underset{}{\overset{\|}{C}}}\!\!\!\!-\bigcirc\!\!\!\!\overset{COO^{\ominus}}{}$$

HOCH$_2$CH$_2$O-C... C-OCH$_2$CH$_2$OH
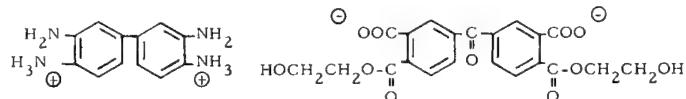
When the reaction time was kept to a minimum at a temperature of
75°C, possibly the reaction did not proceed far beyond the point of salt
formation. The precipitates formed after several hours of reaction,
however, were obviously polymers and not merely a salt of the two
reactants. The product that first precipitated was readily soluble in
dilute aqueous base, indicating that the product at this point had free
carboxyl groups. Also, it was soluble in solvents more polar than EG,
such as DMAc and DMSO. A similar precipitate heated for a longer
time at temperatures up to 100°C was insoluble in all solvents tried,
except concentrated sulfuric acid. This decreased solubility probably
was due to conversion of the polymer to a polyimide structure, in which

the free carboxyl groups are no longer present. No inherent viscosity measurements were attempted in concentrated sulfuric acid since it was felt that the precipitated polymer had been altered during the recovery procedure and the results would not be meaningful at this point.

A polymer that precipitated from a reaction mixture of DAB and BTDA-EG tetraester was insoluble in cold dilute aqueous base but dissolved quickly upon heating. Probably the dissolution was accompanied by the hydrolysis of the ester groups, since the material remained in solution after cooling. The solubility characteristics gave no indication that cyclization occurred to any significant extent.

An indication of the complexity of the polymerization reaction in EG was obtained from the elemental analyses of precipitated polymers. The results are presented in Table VII. Resins D1516-37 and D1516-43 were made from what was assumed to be BTDA-EG diester diacid, while D1516-48 was made from the more fully esterified BTDA-EG system (tetraester). All the products precipitated or gelled in the reaction mixture and were washed repeatedly in methanol and dried thoroughly under vacuum. (It was noted that the washings from D1516-43 turned dark on standing, apparently due to air oxidation of amino compounds.)

Table VII. Elemental Analyses and Mole Ratios
of Precipitated Polymer Powders

Property	Resin System		
	D1516-37	D1516-43	D1516-48
Percent carbon	63.17	62.22	60.62
Percent hydrogen	4.56	4.83	5.73
Percent nitrogen	8.29	7.64	5.88
Percent oxygen (by difference)	23.98	25.31	27.77
Moles DAB/mole BTDA	0.92	0.89	0.86
Moles EG/mole BTDA	2.31	3.08	7.06
Moles H_2O removed/ mole BTDA	2.32	2.82	6.85

The analyses indicated the polymers were all lower than theoretical in nitrogen and higher than theoretical in hydrogen. A more detailed analysis of the results was made by setting up four equations for each polymer (P) as follows. (The percentage of oxygen in these analyses was obtained by difference.)

$$\frac{\% \text{ C in BTDA}}{100} x + \frac{\% \text{C in DAB}}{100} y + \frac{\% \text{C in EG}}{100} g = \frac{\% \text{C in P}}{100}$$

$$\frac{\% \text{ N in DAB}}{100} y = \frac{\% \text{N in P}}{100}$$

$$\frac{\% \text{H in BTDA}}{100} x + \frac{\% \text{H in DAB}}{100} y + \frac{\% \text{H in EG}}{100} g + \frac{\% \text{H in HOH}}{100} w = \frac{\% \text{H in P}}{100}$$

$$\frac{\% \text{O in BTDA}}{100} x + \frac{\% \text{O in EG}}{100} g + \frac{\% \text{O in HOH}}{100} w = \frac{\% \text{O in P}}{100}$$

These equations then were solved simultaneously to obtain x, y, g, and w (the weight fraction of each in the polymer). This analysis assumes that all possible polymer structures are derived from some chemical or physical combination of BTDA, DAB, and EG accompanied by the elimination of water in certain reactions. As anticipated, the weight fraction of water (w) was a negative quantity in each case.

The results of these analyses are expressed in Table VII as the moles of each component per mole of BTDA. The reliability of these values has not yet been established, but certain general conclusions appear to be justified. First, there is an unexpectedly large amount of EG or EG derivative in each polymer; the amount is highest in that derived from the tetraester. The amount present in the polymer, however, far exceeds the amount (4 moles) theoretically present in the tetraester itself. Second, in all cases the BTDA moieties exceed the DAB moieties. The BTDA/DAB ratio is 1.12 (±3 percent) for all three polymers. The ratio of reactants could have been modified, however, by washing out the more soluble components, if these were

rich in amine content. Third, the number of moles of water lost is almost the same as the number of moles of EG moieties present — the ratio of EG to H_2O being 1.04 (±5 percent) for all cases. This similarity would be anticipated if the glycol is all present in the ester form (except for those ester groups formed by reaction with the anhydride), but it is also true when the amount of glycol far exceeds the amount theoretically allowed. Moreover, the water loss calculated for the tetraester polymer exceeds that assumed for a fully cured Pyrrone (4 moles/mole of BTDA).

After this initial series of BTDA-DAB-EG resins was analyzed, a series of tetraester resins which had been reacted to various end point viscosities was subjected to various analytical tests. The viscosity data for this series of resins are presented in Table IV.

A series of powders was obtained from these same four resins by precipitation of the respective resins in distilled water. Methanol was first tried as the precipitation medium but it was found that resin D1516-59 was slightly soluble so the precipitations were conducted in water. All the products were thoroughly washed with water to remove the ethylene glycol and then dried.

In addition to precipitation of resin D1516-59, a 30-gram sample of the resin was cured by heating from 350 to 650°F in an argon atmosphere at a heating rate of 50°F per hour. The resultant shiny black glossy slab was crushed into smaller pieces and submitted for elemental analysis and differential thermal analysis. All four of the precipitated resins were submitted for elemental analysis, two for molecular weight determinations and one for NMR analysis.

Molecular weight determinations were made on the precipitated polymers D1516-59 and D1516-61 by vapor pressure osmometry in dimethylformamide. The corresponding resins were those with the lowest and the highest viscosities in the series, and molecular weight values of 1450 and 1140, respectively, were obtained. The difference in these values probably reflects differences due to fractional precipitation rather than real differences in the average molecular weights of the reaction products. These molecular weights correspond

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approximately to an oligomer derived from two molecules of BTDA and two molecules of DAB.

Elemental analysis of the polymers gave the results shown in Table VIII. Mathematical analysis of these results according to the procedure described on the preceding pages indicated that only 0.5 to 0.7 mole of DAB was combined with each mole of BTDA. This low DAB content can be explained as being the result of fractionation in the process of isolating the polymers by precipitation, the DAB-rich products being more soluble than precipitated polymer. Furthermore, the analysis suggested that the polymers contained about 7 or 8 moles of bound EG per mole of BTDA and lost a slightly larger amount (about 8 to 11 moles) of water per mole of BTDA present. The only readily apparent

Table VIII. Elemental Analyses of Precipitated and Cured Polymers

Property	Precipitated Polymers				Cured Polymer
	D1516-59	D1516-60	D1516-61	D1516-62	D1516-59C
Percent C	60.67	60.70	60.91	60.72	76.32
Percent H	5.80	5.42	5.37	5.31	5.22
Percent N	4.87	5.08	4.59	3.50, 3.51	4.47
Percent O	28.90	26.78	25.82	26.26	7.61
Percent Ash*	0.20	-	-	0.32	-
Moles DAB/ mole BTDA	0.7047	0.7072	0.6533	0.4902	0.8724
Moles EG/ mole BTDA	7.748	6.965	7.800	8.336	21.007
Moles H_2O lost/mole BTDA	7.851	7.875	9.731	10.829	43.812

*No ash was observed in any of the combustions carried out in the usual microanalysis. The ash found for two samples in separate determinations was below the level at which qualitative detection of a residue can be made in a combustion analysis.

polymer structure which could be derived by attaching these large quantities of EG to the polymer with an equivalent loss of water is shown below:
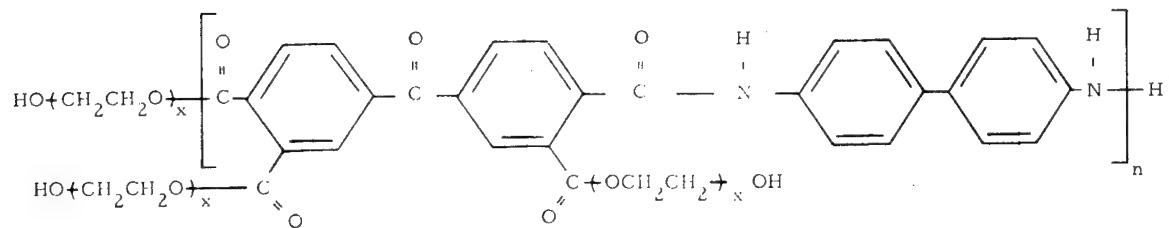
If the above structure were indeed an appropriate representation of the polymers, the polyethylene glycol moieties probably would be lost during cure, and the anticipated Pyrrone structure would be obtained. To determine if such groups were lost, a portion of the original D1516-59 resin, therefore, was heated under argon in a temperature-programmed oven to 650°F to simulate the usual cure cycle, and the cured D1516-59 resin was analyzed. The results, which are shown also in Table VIII, are complicated by the fact that the total carbon, hydrogen, nitrogen and oxygen found was only 93.6 percent of the sample weight. The material which has not been accounted for is probably not carbon, since the carbon found already exceeds that calculated for Pyrrone. It is clear, however, that the hydrogen content is higher and the nitrogen content is lower than anticipated for the Pyrrone structure.

Mathematical analysis of the results indicated that the DAB-BTDA mole ratio was still less than 1, although in this case no fractionation of the polymer could have occurred. An astonishingly large amount of EG (21 moles per mole of BTDA) appeared to be combined in the polymer. In contrast to the precipitated polymers which lost about 1 mole of water for each mole of EG combined, the cured polymer lost 2 moles of water for each mole of EG reacted. In fact, if 2 moles of water were lost for

each mole of DAB in condensation to the Pyrrone, the ratio of additional water lost to EG combined was almost exactly 2 (actually 2.003).

If the cured polymer indeed contained as much EG as indicated, the polymer yield should have been twice the theoretical yield. This possibility was checked with resin D1516-65. A weighed quantity of resin was heated in a cure cycle to 700°F, weighed, heated to 850°F, and weighed again. At 700°F the weight of cured polymer was 106 percent and at 850°F it was 95 percent of the theoretical weight of cured Pyrrone. Some approximations of the resin solids were involved in this experiment, but it seems clear that the cured polymer does not contain substantial amounts of EG moieties.

Since the apparent EG content is not the result of reactions with EG, it must be the result of reactions which produce the same effect in the mathematical analysis. The addition of 1 mole of EG and the loss of 2 moles of water is equivalent to adding 1 mole of vinylene (- CH = CH -) groups. A similar effect could be achieved by the elimination of nitrogen- and oxygen-containing groups, but a likely method of arriving at the observed elemental composition in this manner is not yet apparent.

The NMR spectrum of the precipitated D1516-59 polymer was obtained from a solution of the polymer in deuterated dimethylsulfoxide. Only the region from 1.7 to 10 τ was covered. The complex spectrum contained three distinct regions of absorption: A, 1.7 to 2.7τ, 20.8 percent of the total hydrogen absorbance; B, 2.9 to 3.8τ, 8.6 percent; and C, which consisted of a series of peaks, 5.1 to 7.1τ, 70.6 percent. A corresponds to absorption by aromatic hydrogens ortho to carbonyl groups, and B is in the region anticipated for aromatic hydrogens on amino-substituted rings. The series of peaks in C probably results from a combination of absorption by - CH_2O -, $ArNH_2$, and - OH hydrogens. Amide hydrogens probably are included in A. $ArNH_3{}^+$ and $ArCOOH$ hydrogens, if any were present, would have fallen outside the test region. Using the above assignments and assuming that the polymer was the fully esterified oligomer derived from 2 BTDA and 2 DAB molecules, the calculated ratio of A:B:C should have been 1.33:1:2.92, and C/A should have been 2.19. The observed values for A:B:C were 2.42:1:8.22, and

C/A was 3.39. NMR evidence, therefore, supports the elemental analysis in a qualitative fashion, both methods indicating that the DAB/BTDA ratio is considerably less than one and that the content of EG moieties was greater than anticipated.

Two samples of polymer powder derived from resin D1516-59 were prepared and subjected to differential thermal analysis. The first sample was obtained by precipitation of the polymer in water and the second by curing a portion of D1516-59 resin in an argon atmosphere to a maximum temperature of 650°F.

The precipitated polymer exhibited three reproducible endotherms below 200°C. These are found at 75, 125 and 155°C. Just above 200°C the sample apparently loses weight (ΔT noise) by means of volatilization, and beyond 300°C the decomposition becomes more pronounced. No transitions were observed above 500°F. The three endotherms below 200°C are well defined and are probably the temperatures at which volatile components are lost from the uncured powder. The instability of the uncured powder is indicated by the relatively low temperatures at which initial decomposition occurs.

The D1516-59 resin cured in an argon atmosphere shows several ΔT spikes at approximately 100°C which are probably caused by a loss of volatiles. At about 150°C the sample begins to evolve heat and the baseline shifts in a positive direction. At about 380°C the slope changes and continues to a peak at 493°C. This curve illustrates the stability of the cured polymer when run in an inert atmosphere. The cured material apparently is not subject to thermal degradation at temperatures below 500°C. The absence of any transitional peaks confirms that the polymer is in a highly cured condition.

No further characterizations of the BTDA-DAB-EG tetraester type resins were conducted until standard resin BED-2 was prepared. The efforts during this interim period were directed at improvement of the processing variables, synthesis scale up and mechanical strength properties rather than chemical characterization. Upon selection of the BED-2 resin as the standard BTDA-DAB-EG tetraester resin, a sample was cured in an argon atmosphere from room temperature to 700°F over

a 9-hour period. This cured BED-2 resin was ground to pass a No. 80
U. S. Standard Sieve and part of this sample was subjected to thermo-
gravimetric analysis in static air at a heating rate of 5°C per minute.
The results of this analysis are shown in Figure 5. The resin demon-
strates a reasonable degree of thermal stability to approximately 300°C
but degrades rather rapidly at higher temperatures.
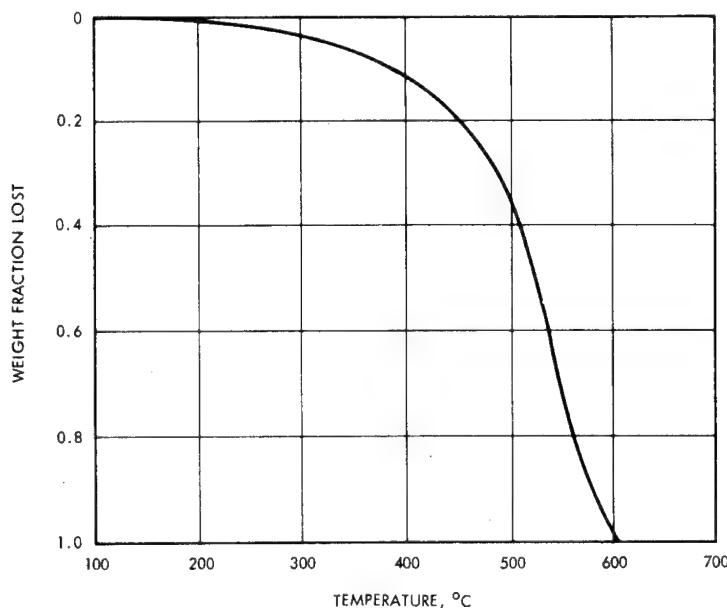
Figure 5.   Thermogravimetric Analysis of
Cured BED-2 Resin

Infrared absorption analysis was run on a nominal 1 mil thick film
of BED-2 resin. The BED-2 resin was heated at 300°F to form a very
viscous fluid and this fluid was introduced to a heated press between two
sheets of Teflon. The resin film was heated to 500°F and held for 1/2
hour at contact pressure, cooled to room temperature and stripped from
the Teflon. The infrared absorption spectrum of this film is shown in
Figure 6. After the spectrum of the BED-2 film (cured at 500°F) had
been run, the film was postcured from 300° to 700°F in an argon atmos-
phere and another infrared spectrum was obtained. The infrared spec-
trum of the postcured BED-2 film is shown in Figure 7.

Examination of Figures 6 and 7 indicates that both the cured and
postcured BED-2 resin films exhibit a high degree of imide character

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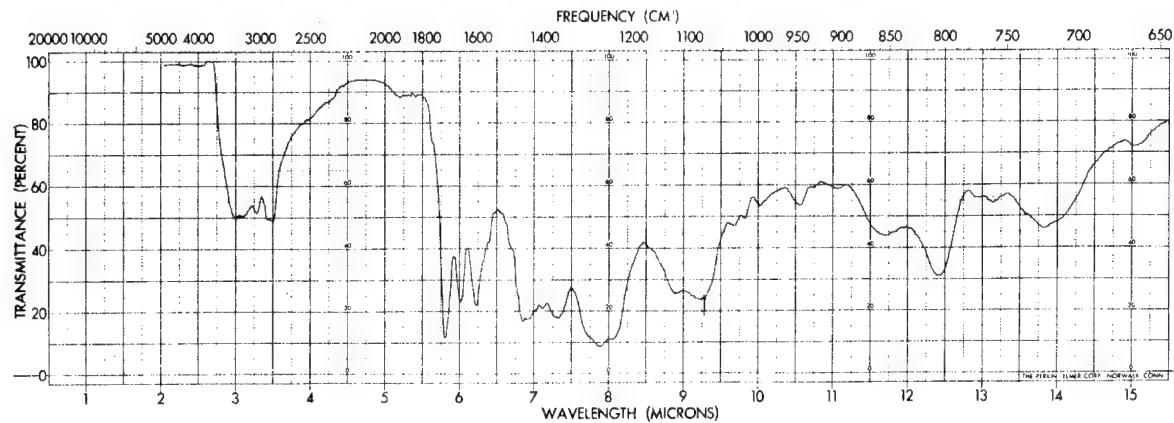
Figure 6. Infrared Spectrum of Cured BED-2 Resin
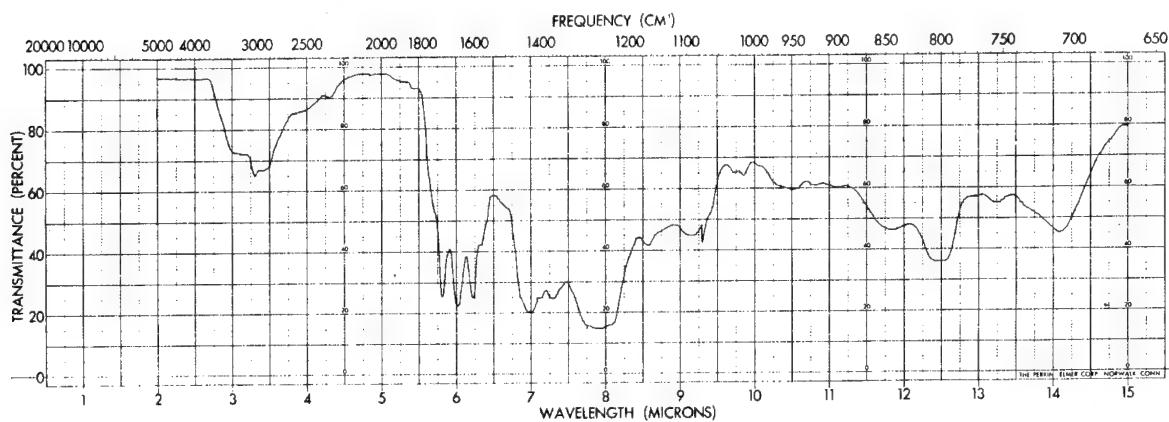
Figure 7. Infrared Spectrum of Postcured BED-2 Resin

with very little evidence to confirm the presence of the imidazopyrrolone structure (ref. 4, 8, 12). The 1760 cm^{-1} and 1735 cm^{-1} absorption bands attributed to the imidazopyrrolone are noticeably absent in the spectra of Figures 6 and 7. Close examination of the postcured BED-2 resin spectrum (Figure 7) shows a slight indication of the appearance of a 1760 cm^{-1} shoulder on the stronger 1720 cm^{-1} imide carbonyl band, however, this band is overshadowed by the much more intense absorption attributed to imide character.

This evidence, along with the increasing intensity of the 1775 cm^{-1} shoulder and the 720 cm^{-1} absorption bands, when progressing from the cured to the postcured resin, confirm the strong imide character of the films. The absence of the C=N imidazole stretching vibration at

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1620 cm^{-1} also indicates the amount of imidazopyrrolone structure to be minimized in the cured resin.

Viscosity Measurements

The BTDA-DAB polymer synthesized in ethylene glycol and concentrated to 30 percent solids was subjected to viscosity measurements in an Ostwald-Fenske viscometer at 25°C.

It became apparent at a concentration of 0.157 gm/dl that the viscosity study would have to be curtailed since the average efflux time was less than that of the pure solvent. At this time, the only explanation for this phenomenon is that the hygroscopic nature of the ethylene glycol caused a dilution of the resin by water absorption.

Another interesting phenomenon was that of a curdling which occurred when the 30 percent resin was diluted to a concentration of 3.56 gm/100 ml. The dilution was accomplished by adding 10 ml of the 30 percent resin to a 100 ml volumetric flask and adding pure ethylene glycol to the reference mark. Upon shaking the flask lighter colored curds of material appeared in the dark solution. Throughout the viscosity run the diluted resin had the appearance of a suspension rather than a true solution (i.e., turbid rather than clear) indicating that the curds did not re-dissolve but were stable in dilute solution. The dilute solution was heated also to 50°C with shaking and did not appear to clear up. The reason for this this behavior was not determined and the viscosity study was curtailed at this point.

Dynamic Modulus

An attempt was made to determine the viscoelastic behavior of the same resin, using the vibrating reed technique.

Three dip coats were coated on substrates of stainless steel, beryllium-copper and a three-ply glass cloth-resin laminate with drying at 130°F between coatings. No distinctive change in dynamic modulus was observed when the reeds were heated from ambient to 580°F. Examination of the reeds after heating to 580°F showed a tough

dark colored skin on the surface of the hardened resin and a yellow foam-like underlying layer. It appears that the resin at the surface can readily lose the ethylene glycol to form a very hard dense skin which in turn prevents the loss of the glycol from the resin beneath the resultant skin. This foam-like material has very poor adhesion to the reed substrate material with the net result that any change in dynamic modulus that occurs cannot be detected because the fundamental frequency of the system is not shifted to any appreciable degree.

Another effort was attempted to detect a change in dynamic modulus by loading the surface of the glass cloth three-ply laminate with the fluid resin and heating this system. The glass cloth laminate substrate appears to be the most sensitive to changes in modulus but the adhesion problem will have to be solved before reliable data with no discontinuities can be developed.

Cure Plate Gel Times

The "gel" times of both a 30 percent solids BTDA-DAB-EG resin and a 20 percent solids PMDA-DAB-EG resin were determined using the cure plate method. In this method, several drops of the resin were dropped onto a hot plate at the temperature of interest and were repeatedly squeezed between the hot plate and a spatula until threads of polymer began to form. The threads were stretched repeatedly until the material became too viscous to form anymore threads. From the time the resin first touched the hot plate until the material no longer formed threads was recorded as the "gel" time.

These times gave a good indication of the period during which the respective resins possessed reasonable flow characteristics and thus were conducive to optimum laminate formation. The BTDA-DAB-EG resin tested had "gel" times which varied from 172 seconds at 250°F to 24 seconds at 350°F while the PMDA-DAB-EG resin had times which varied from 280 seconds at 250°F to 43 seconds at 350°F.

The "gel" time also served as a method for checking the stability
of the resins. Since BTDA-DAB-EG resin D1516-53 appeared to be one of
the better resins and was used to form several laminates, it was selected
for a stability study. The "gel" time of this resin was determined at
450, 475, and 496°F. A portion of the resin was allowed to stand at
room temperature for 11 days in a closed container. This resin had
"gel" times of 100, 69 and 46 seconds originally for the respective 450,
475 and 496°F temperatures. A recheck of the D1516-53 resin after
11 days showed no change of "gel" times thus indicating no significant
advancement of the resin at room temperature.

4.3 LAMINATING AND PHYSICAL PROPERTIES

A series of glass cloth laminates was molded from various types
of BTDA-DAB resins that had been synthesized in ethylene glycol. The
initial BTDA-DAB-EG resins were synthesized under rather mild reac-
tion conditions and were considered to be of the diacid-diester type.
The latter laminates were molded from the more fully esterified resins
that were designated as the tetraester type. The knowledge gained from
the Phase I laminating program along with DTA analysis of the ester
type material was put to good use; the net result was the formation of a
greater number of successful laminates. The same criteria were used
to judge the usefulness of the particular resin system under evaluation.
These criteria were flexural strength and modulus, retention of room
temperature strength at elevated temperatures, and volume percent
voids in the resin matrix. A description of the particular behavior of
the resins used for laminating purposes and a description of the
laminates formed from resins of the BTDA-DAB-EG type are described
in the following sections.

NASA-Langley BTDA-DAB-EG Resin

During Phase I the laminate that exhibited the greatest flexural
strength was shown to be molded with a BTDA-DAB type resin. This
observation along with the suspected degradation of the laminates as a
result of detrimental polymer-solvent interaction led to evaluation of

BTDA-DAB type resins synthesized in ethylene glycol. The results of an investigation of this type resin synthesized at 33 percent solids by NASA - Langley are given in Table IX.

Two laminates were formed from the BTDA-DAB-EG resin submitted by NASA - Langley, under conditions similar to the formation of Phase I laminates. Although no drastic changes occurred in the laminating conditions, there was an immediate improvement of flexural strengths and moduli. Flexural strengths on the order of 60,000 psi and moduli as high as 5×10^6 psi were achieved with the NASA resin. Since this BTDA-DAB-EG resin demonstrated a marked improvement in the physical properties of laminates formed from it, synthesis of this type resin was initiated at Hughes. Several resins of the BTDA-DAB-EG type designated D1516-35 and D1516-36 were synthesized.

Hughes Diacid-Diester BTDA-DAB-EG Resins

A laminate was formed using prepreg which had been dried at 180°F for 45 minutes in a forced draft oven. The physical properties of this laminate are recorded in Table IX along with the conditions under which it was formed. The strength of this laminate was rather disappointing, thus the drying conditions of the prepreg were changed from 180°F drying in a forced draft oven to 170°F drying in a vacuum oven and 1500 psi pressure in the press. This treatment of the material resulted in much improved strength properties. Drying conditions of 180 and 160°F in a vacuum oven were tried for several laminates. Drying at 180°F in a vacuum oven resulted in better strength properties than the 160°F drying. The pressure also was dropped to 1250 psi to reduce resin "squeeze out".

Hughes PMDA-DAB-EG Resin

A PMDA-DAB-EG resin was synthesized following the same procedure used to produce the BTDA-DAB-EG resins. A laminate was

Table IX. BTDA-DAB-EG and PMDA-DAB-EG Laminate Properties for Initial Phase II Program

Laminate Designation (1)	Resin Designation (2)	Laminating Conditions			Final Resin Content percent	Density, gm/cc	Volume Percent Voids in Resin percent	Average Flexural Strength (psi x 10⁻³)		Average Modulus (psi x 10⁻⁶)		Remarks
		Contact Time, minutes	Maximum Pressure, psi	Temp. Range, °F				Room Temp.	Elevated Temp.	Room Temp.	Elevated Temp.	
PF-35	NASA-Langley	3[4]	200	275-600	25.5	1.52	46.7	68.1	42.4[8] / 39.0[9]	3.25	2.42[8] / 2.35[9]	Laminate non-uniform in appearance
PF-37	NASA-Langley	3[4]	1500	275-600	12.4	1.91	47.8	59.9	49.6[8] / 52.2[9]	5.12	4.76[8] / 5.18[9]	Varnish wet cloth thoroughly
PF-41	D1516-35	0[4]	1000	275-600	24.9	1.61	41.8	33.9	35.6[10] / 6.9[10]	2.69	2.96[10] / 1.72[10]	Edges porous and surface mottled
PF-42	D1516-35	0[5]	1500	275-600	27.8	1.73	28.0	62.8	43.1[10] / 12.3[10]	3.90	3.12[10] / 2.46[10]	Laminate had a uniform appearance
PF-43	D1516-36	0[5]	1250	250-600	31.3	1.71	24.2	63.8	33.5[10] / 37.6[10]	3.78	2.65[10] / 2.89[10]	Laminate was solid and appeared uniform
PF-44	D1516-36	0[5]	1250	250-600	17.3	1.84	40.0	44.9	34.0[10] / 14.1	2.34	2.09[10] / 1.97[10]	Laminate showed good resin squeeze out
PF-45	D1516-38[3]	2-1/2[5]	1250	275-600	19.3	1.83	36.1	57.2	43.1[10] / 9.3[10]	4.39	4.06[10] / 3.10[10]	Laminate felt solid and had good edges
PF-46	D1516-36	0[5]	1250	275-600	32.9	1.70	26.6	56.4	38.0[8] / 38.3	*	*	Indication of slight edge delamination
PF-47	D1516-36	1-1/2[5]	1250	275-600	22.4	1.77	38.2	75.2	63.3[8] / 49.8[9]	*	*	Laminate showed good resin flow
PF-48A[6]	D1516-36	0[5]	1250	275	23.3	1.85	30.3	67.4	47.5[9]	*	*	-
PF-48AR[7]	D1516-36	0[5]	1250	275	26.2	1.82	27.6	71.3	49.7[9]	*	*	-
PF-49A[6]	D1516-36	0[5]	1250	275-350	18.6	1.87	38.2	54.1	43.6[9]	*	*	-
PF-49AR[7]	D1516-36	0[5]	1250	275-350	16.7	1.88	41.8	65.5	47.9[9]	*	*	-
PF-50A[6]	D1516-36	0[5]	1250	275-425	19.6	1.73	46.4	46.2	33.8[9]	*	*	-
PF-50AR[7]	D1516-36	0[5]	1250	275-425	21.6	1.79	38.3	64.5	42.9[9]	*	*	-
PF-51A[6]	D1516-36	0[5]	1250	275-500	22.6	-	-	54.9	42.8[9]	*	*	Could not get voids and density due to blister
PF-51AR[7]	D1516-36	0[5]	1250	275-500	24.4	1.72	38.4	61.4	33.2[9]	*	*	-

(1) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish
(2) All laminates were of the BTDA-DAB-EG type resin with the exception of PF-45
(3) Laminate PF-45 was fabricated using PMDA-DAB-EG resin
(4) Prepreg conditioned for 45 minutes at 180°F in air
(5) Prepreg conditioned in a vacuum oven between 160-180°F
(6) Laminate was postcured to 600°F over 50 hours in air

(7) Laminate was postcured to 600°F over 50 hours in argon
(8) After 1/2 hour at 400°F
(9) After 1/2 hour at 600°F
(10) After 1/2 hour at 700°F
* Data not available due to instrumentation difficulties

formed from a resin of approximately 20 percent concentration under conditions of pressure and temperature identical to those used to form the BTDA-DAB-EG laminates. The results of this investigation indicate an appreciable increase in strength over the PMDA-DAB-DMAc systems investigated in the Phase I laminating studies. This verifies the prediction that the improved flow characteristics to be expected from resins synthesized in esterifying solvents would result in improved strength. Examination of the physical properties of PF-45 recorded in Table IX indicate that these improved strength characteristics were achieved.

Staged Heating in Press

Several laminates were formed under similar conditions of pressure and temperature with the press temperature increased step-wise during the molding operation. One prepreg was dried 2 hours at $180^{o}F$ in a vacuum oven while the other prepreg was dried for 1-1/2 hours at $180^{o}F$ in the vacuum oven. The resultant differences in strength properties due to this variation in the drying treatment are recorded in Table IX. The shorter drying period used for PF-47 prepreg resulted in a much higher strength in the laminate. This indicates that the ultimate strengths to be developed in laminates formed from this type resin system are very sensitive to the treatment given the prepreg material.

Combined Effects of Press Temperature and Postcure

At this point in the investigation, since a systematic study of the effects of press temperature and postcuring in both air and argon appeared to be warranted, an experiment was set up.

Each prepreg was prepared by applying three spatula coats of 30 percent BTDA-DAB-EG resin to style 181 glass cloth with an A1100 finish. Each successive coating was dried for 15 minutes at $180^{o}F$ and

the prepreg was cut into 6 x 8 inch plies. These plies were held at 180°F in a 28.5-inch vacuum for 105 minutes. The vacuum oven-dried plies were used to form four 6 x 8 inch - 12-ply laminates. These four laminates were introduced into a press at 275°F and 1250 psi pressure was applied. The press temperatures were varied from 275 to 500°F at 75°F increments to give four temperature conditions.

Upon completion of the pressing stage the finished laminates were cut into two equal halves and the halves postcured in either air or argon by a programmed heating cycle which increased the temperature from 275 to 600°F over a 48-hour period. The laminates were held at 600°F for 2 hours, allowed to cool to below 200°F and removed for further testing.

After completion of the postcuring, the finished laminates were cut into specimens for flexural strength and modulus determinations. The results of these tests are recorded in Table IX for laminates PF-48A and PF-48AR through PF-51A and PF-51AR. Close examination of the physical properties for this series of eight laminates indicates that the best strength properties are achieved by a maximum press temperature of 350°F, and in all cases the argon postcure gives higher strength laminates than the air postcure. The physical properties of the BTDA-DAB-EG laminates postcured in air and argon are recorded in Table IX.

Resins of Higher Concentration

In an effort to determine the effect of resins synthesized at higher concentrations rather than concentrated by distilling off solvent, laminates were formed from two Hughes synthesized resins. A series of four laminates was formed at maximum press temperatures of 250 and 275°F and a 1250 psi pressure. These laminates then were given a 50-hour postcure in argon to a maximum temperature of 600°F. Following these procedures decreased strengths below previous strength values, thus resins synthesized at high solids concentrations did not

appear to produce improved laminates. The physical properties and strengths obtained for these four laminates are recorded in Table X.

Tetraester Resins Synthesized below Reflux Temperatures

A series of laminates was formed using resins prepared by reacting a previously prepared BTDA-EG ester with DAB at temperatures lower than reflux. This type of resin was thought to contain BTDA which had been reacted to the tetraester form, thus all subsequent resins are referred to as tetraester resins. The details of the individual syntheses are documented in Section 4.1.

This series of laminates was formed using resins D1516-46 through D1516-51, with the exclusion of D1516-48, which was too viscous to treat in the same manner as the other more fluid resins. All five resins used to form these laminates were of the more fully esterified type. Early in the investigation, it was found that these resins possessed much better flow characteristics than those BTDA-DAB-EG resins produced without water removal during the esterification process. A series of 2 x 2-inch test laminates were run using resin D1516-46 to determine the conditions necessary to minimize squeeze-out in the press during lamination.

As a result of this preliminary study, the drying of the prepregs was conducted at 225°F for either 25 or 15 minutes after each coat was applied to the glass cloth. The vacuum oven drying was discontinued and the prepregs were "B" staged for 5 minutes at 400°F prior to the laminating operation. Even with this more rigorous treatment of the prepregs it was found that long contact times at 450°F were necessary in the press to minimize resin squeeze-out. Since all but one of the five laminates delaminated in postcure, it appears that the laminates still contain a large amount of volatile material. This observation in conjunction with DTA data indicated that more vigorous drying and "B" staging of the prepreg as well as increased press temperatures would have to be used to eliminate the volatile material before postcure. Table X summarizes the behavior of laminates PF-56 through PF-60.

Table X. BTDA-DAB-EG Laminate Properties for Initial Phase II Program

Laminate Designation (1) (2)	Resin Designation	Laminating Conditions			Final Resin Content, percent	Density, gm/cc	Volume Percent Voids in Resin, percent	Average Flexural Strength (psi x 10^-3)		Average Modulus (psi x 10^-6)		Remarks
		Contact Time, minutes	Maximum Pressure, psi	Temp. Range, °F				Room Temp.	Elevated Temp.	Room Temp.	Elevated Temp.	
PF-52[7]	D1516-41	2[3]	1250	275	27.1	-	-	-	-	-	-	Specimen delaminated during postcure
PF-53[7]	D1516-42	3[3]	1250	275	27.8	1.73	31.2	58.7	52.4[9] 43.7[10]	*	*	Laminate had a uniform appearance
PF-54[7]	D1516-41	2[3]	1250	250	20.2	1.83	37.0	56.5	52.5[9] 42.2[10]	*	*	Laminate had a uniform appearance
PF-55[7]	D1516-42	3[3]	1250	250	24.2	1.74	36.4	42.7	38.5[9] 30.4[10]	*	*	Laminate had a uniform appearance
PF-56[7]	D1516-46	6-1/2[5]	1250	450	25.3	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-57[7]	D1516-47	5[5]	1250	450	28.2	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-58[7]	D1516-49	5[5]	1250	450	24.0	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-59[7]	D1516-50	5-1/2[5]	1250	450	21.5	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-60[7]	D1516-51	5-1/2[5]	1250	450	18.2	1.84	40.6	51.3	49.5[9] 39.2[10]	*	-	Laminate had a uniform appearance
PF-61[8]	D1516-53	1[5]	1250	500-700	23.7	1.84	29.3	58.9	50.6[10]	4.53	4.32[10]	
PF-62[8]	D1516-53	4[5]	1250	400-650	18.0	1.93	33.5	72.4	56.8[10]	5.35	5.11[10]	
PF-63[8]	D1516-53	3-1/2[6]	1250	400-650	25.6	1.86	24.1	70.2	56.1[10]	4.52	4.51[10]	
PF-64[8]	D1516-55	4[4]	1250	400-600	23.4	1.78	34.8	52.3	52.5[10]	4.54	4.52[10]	
PF-65[8]	D1516-53	-	15	350-450	17.8	1.56	59.2	63.8	52.8[10]	4.28	4.02[10]	Laminate formed by vacuum bag technique

(1) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish
(2) All laminates were fabricated using BTDA-DAB-EG type resin
(3) Prepreg was conditioned in a vacuum oven at 180 F
(4) Prepreg was conditioned at 225°F and "B" staged at 300°F
(5) Prepreg was conditioned at 225°F and "B" staged at 400°F
(6) Prepreg was conditioned at 225°F and "B" staged at 500°F
(7) Laminate was postcured to 600°F over 50 hours in argon
(8) Laminate was postcured to 700°F over 17 hours in argon
(9) After 1/2 hour at 400°F
(10) After 1/2 hour at 600°F
* Data not available due to instrumentation difficulties.

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Tetraester Resins Synthesized at Reflux Temperatures

Since BTDA-DAB-EG resin D1516-51 was the only resin which formed a successful laminate in the previous series, and was the only one of the resins used which had been reacted at reflux, a series of four laminates was formed using resins of the tetraester type which were reacted at reflux temperatures to the desired viscosity. The results obtained from this series of laminates are detailed in Table X. This series of laminates indicated that laminates with flexural strengths above 70,000 psi and moduli on the order of 5×10^6 psi could be achieved with the tetraester type resins when the proper drying and "B" staging conditions were used. At this time it appeared that the optimum press temperatures for this type of resin were approximately 650°F. Since the tetraester type resins produced relatively high strengths with preliminary laminating studies, it was probable that these properties could be improved considerably by optimization of the processing conditions.

To ensure applicability of this type of resin to other processing techniques, a vacuum bagged laminate was formed using BTDA-DAB-EG tetraester type resin according to the conditions described in Table X. This laminate was formed at a maximum temperature of 450°F with a subsequent postcure in argon to a maximum temperature of 700°F. This laminate had a flexural strength in the 60,000 psi range and a modulus above 4×10^6 psi. These strengths are very encouraging since they were achieved with a rather low resin content (17.8 percent) and a relatively high volume percent voids (59.2 percent).

Optimization of the BTDA-DAB-EG Resin System

After the laminate was formed, sufficient understanding of the BTDA-DAB-EG resin system had been gained to permit optimization of laminates made from this type of resin. A program was designed wherein close coordination between the synthesis of resins and processing of laminates was attempted. As the results obtained from the processing studies became available, the BTDA-DAB-EG resin synthesis was modified to give more optimum properties to the resins

used for processing studies. By use of this flexible approach to the twofold problem, flexural strength values in the 70,000 to 80,000 psi range and moduli between 3 to 5 x 10^6 psi when desired were achieved in a routine manner. In addition to the consistent improvement of mechanical strength values, the volume percent void level in the laminates was reduced to the 15 to 25 percent range.

In addition to the various modifications made in the polymer synthesis (described in Section 4.1), various modifications in laminate processing also were attempted. This initial optimization program is summarized in Tables XI and XII. In the series of laminates designated PF-66 to PF-95, all laminates were made with the BTDA-DAB-EG type resin with the exception of PF-72 in which a PMDA-DAB-EG resin prepared as described in Section 4.1 was used. All laminates were prepared using style 181 "E" glass cloth with an A-1100 finish except for PF-95 in which heat cleaned style 581 quartz cloth was used.

Laminates between PF-66 and PF-75 in the series used a postcure cycle from 300-700°F over a 17-hour period. All remaining postcure cycles were from 300-850°F over a 58-hour period. All postcure cycles were conducted in an argon atmosphere. All elevated temperature tests were conducted at 600°F after being held at 600°F for 1/2 hour.

By midpoint of the initial optimization study, respectable flexural strengths and moduli were achieved; therefore, several other mechanical strength properties were obtained to determine if they were in line with the flexural strength values. The values obtained for interlaminar shear strength, edgewise compressive strength, and tensile strength are recorded for several laminates at the beginning of Table XII.

The remainder of the initial optimization study was spent determining the conditions necessary to produce a workable resin and the processing conditions necessary to achieve optimum mechanical strength properties. The results of this investigation laid the groundwork for the resin synthesis scale up and reinforcement investigation.

Table XI. BTDA-DAB-EG and PMDA-DAB-EG Laminate Properties for Optimization Program

Laminate Designation[1][2]	Resin Designation	Laminating Conditions			Final Resin Content, percent		Density, gm/cc		Volume Percent Voids in Resin, percent		Average Flexural Strength, psi x 10⁻³		Average Modulus, psi x 10⁻⁶	
		Contact Time, minutes	Maximum Pressure, psi	Temperature Range, °F	As Molded	As Postcured	As Molded	As Postcured	As Molded	As Postcured	Room Temperature	Elevated[8] Temperature	Room Temperature	Elevated[8] Temperature
PF-66	D1516-59	11[5]	1250	400-600	25.5	-	1.87	-	23.4	-	72.1	41.1	-	-
PF-66[4]	D1516-59	11[5]	1250	400-600	-	23.3	-	1.82	-	31.8	65.7	63.9	4.71	4.22
PF-67	D1516-59	6[5]	1250	450-600	21.3	-	1.97	-	22.2	-	79.5	48.5	-	-
PF-67[4]	D1516-59	6[5]	1250	450-600	-	19.7	-	1.92	-	30.6	70.6	61.0	5.22	4.92
PF-68	D1516-62	0[5]	1250	450-600	33.8	-	1.80	-	16.6	-	59.8	32.0	-	-
PF-68[4]	D1516-62	0[5]	1250	450-600	-	31.4	-	1.75	-	24.2	56.5	47.8	3.92	3.63
PF-69	D1516-60	2[6]	1250	450-600	29.9	-	1.82	-	20.5	-	68.4	41.9	-	-
PF-69[4]	D1516-60	2[6]	1250	450-600	-	27.3	-	1.82	-	24.7	68.7	57.0	4.11	3.79
PF-70	D1516-60	[7] resin "washed out" due to excessive flow												
PF-71	D1516-61	0[5]	1250	450-600	33.2	-	1.76	-	20.8	-	58.9	34.4	-	-
PF-71[4]	D1516-61	0[5]	1250	450-600	-	30.9	-	1.71	-	28.1	55.0	49.4	3.78	3.73
PF-72	D1516-63[3]	4[5]	1250	450-600	27.8	-	1.82	-	23.9	-	73.0	50.7	-	-
PF-72[4]	D1516-63[3]	4[5]	1250	450-600	-	25.2	-	1.77	-	32.4	61.6	54.3	4.35	*
PF-73	D1516-65	0[5]	1250	450-600	33.9	-	1.72	-	27.2	-	50.2	49.0	-	-
PF-73[4]	D1516-65	0[5]	1250	450-600	-	31.9	-	1.68	-	28.7	57.7	48.7	2.99	2.51
PF-74	D1516-65	3[5]	1250	450-600	27.3	-	1.87	-	20.3	-	71.6	52.5	-	-
PF-74[4]	D1516-65	3[5]	1250	450-600	-	25.5	-	1.82	-	27.8	62.5	61.1	3.48	3.10
PF-75	D1516-65	2-1/2[5]	1250	450-600	24.5	-	1.86	-	26.1	-	74.8	49.9	-	-
PF-75[4]	D1516-65	2-1/2[5]	1250	450-600	-	23.0	-	1.85	-	29.8	63.7	63.0	3.65	3.47
PF-76	D1516-65	4[5]	1250	450-800	18.5	-	1.86	-	38.3	-	66.9	59.9	4.20	3.58
PF-77	D1516-65	3[5]	1250	450-700	27.8	-	1.83	-	23.0	-	72.6	59.5	3.57	2.87
PF-78	D1516-65	3[5]	1250	450-650	28.8	-	1.82	-	22.3	-	77.0	52.4	3.57	4.16
PF-79	D1516-65	3[5]	1250	450-750	26.0	-	1.85	-	24.3	-	58.4	53.7	3.70	4.24

(1) All laminates were fabricated with style 181 "E" glass cloth with an A-1100 finish

(2) All laminates fabricated with BTDA-DAB-EG resin except PF-72

(3) Laminate PF-72 fabricated with PMDA-DAB-EG resin

(4) Laminate postcured to 700°F over 17 hours in argon

(5) Prepreg conditioned at 225°F and "B" staged at 400°F

(6) Prepreg conditioned at 225°F and "B" staged at 450°F

(7) Prepreg conditioned at 225°F with no "B" staging

(8) Tested at 600°F after 1/2 hour at 600°F

*Data not available due to instrumentation difficulties

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Table XII. BTDA-DAB-EG Laminate Properties for Optimization Program

Laminate Designation[1][2]	Resin Designation	Laminating Conditions			Final Resin Content, percent		Density, gm/cc		Volume Percent Voids in Resin, percent		Average Flexural Strength, psi x 10^{-3}		Average Modulus, psi x 10^{-6}	
		Contact Time minutes	Maximum Pressure, psi	Temperature Range °F	As Molded	As Postcured	As Molded	As Postcured	As Molded	As Postcured	Room Temperature	Elevated[10] Temperature	Room Temperature	Elevated[10] Temperature
PF-80	D1516-68	3-1/2[5]	1250	450-700	25.4	-	1.88	-	22.7	-	1467[7]	985[7]	-	-
PF-81	D1516-68	3-1/2[5]	1250	450-700	24.6	-	1.87	-	25.0	-	38.3[8]	22.0[8]	4.26	3.66[8]
PF-82	D1516-68	3-1/2[5]	1250	450-700	22.8	-	1.88	-	27.6	-	49.0[9]	41.7[9]	3.94	2.88[9]
PF-83	D1516-65	4[5]	1250	450-700	22.7	-	1.86	-	29.5	-	78.5	58.0	5.89	4.79
PF-84	D1516-70	5[5]	1250	450-700	26.0	-	1.83	-	26.0	-	77.6	64.5	5.14	4.57
PF-85	D1516-70	1[5]	1250	450-680	31.8	-	1.80	-	19.4	-	-	-	-	-
PF-85[4]	D1516-70	1[5]	1250	450-680	-	27.9	-	1.76	-	28.7	28.9	27.9	4.17	4.05
PF-86[4]	D1516-71	1[5]	1250	450-680	31.9	-	1.79	-	20.1	-	-	-	-	-
PF-86[4]	D1516-71	1[5]	1250	450-680	-	27.6	-	1.76	-	29.2	-	-	-	-
PF-87	D1516-71	3-1/2[6]	1250	450-680	33.2	-	1.82	-	15.7	-	-	-	-	-
PF-87[4]	D1516-71	3-1/2[6]	1250	450-680	-	29.1	-	1.80	-	23.5	33.6	31.6	4.82	4.34
PF-88	D1516-71	3-1/2[6]	1250	450-680	33.7	-	1.77	-	19.3	-	-	-	-	-
PF-88[4]	D1516-71	3-1/2[6]	1250	450-680	-	29.8	-	1.73	-	28.1	27.6	25.3	4.23	3.85
PF-89	D1516-71	3-1/2[6]	1250	450-680	33.3	-	1.77	-	19.8	-	56.0	49.2	5.35	4.14
PF-90	D1516-71	3-1/2[6]	1250	450-680	34.3	-	1.78	-	17.6	-	61.2	45.8	4.75	3.88
PF-91	D1516-71	3[6]	1250	450-680	27.5	-	1.84	-	22.6	-	67.3	51.8	4.99	4.48
PF-92	D1516-80C	4-1/2[6]	1250	450-680	31.8	-	1.74	-	24.4	-	60.0	51.6	4.35	3.91
PF-93	D1516-81B	5-1/2[6]	400	450-680	32.9	-	1.74	-	22.9	-	54.1	48.9	4.03	3.82
PF-94	D1516-81C	5[6]	400	450-680	23.6	-	1.81	-	32.0	-	69.1	50.1	5.14	4.49
PF-95[3]	D1516-81C	4-1/2[6]	400	450-680	23.3	-	1.69	-	43.3	-	24.0	26.7	4.18	4.12

(1)All laminates were fabricated with style 181 "E" glass cloth with an A-1100 finish with the exception of laminate PF-95

(2)All laminates fabricated with BTDA-DAB-EG resin

(3)Laminate PF-95 fabricated with heat cleaned style 581 quartz cloth

(4)Laminate postcured to 850°F over 58 hours in argon

(5)Prepreg conditioned at 225°F and "B" staged at 400°F

(6)Prepreg conditioned at 225°F and "B" staged at 300°F

(7)Interlaminar shear strength (in psi) according to Federal Test Method Standard 406

(8)Edgewise compressive strength (in 10^3 psi) and modulus (in 10^6 psi) according to ARTC Test Method

(9)Tensile strength (in 10^3 psi) and modulus (in 10^6 psi) according to ASTM Method D638

(10)Tested at 600°F after 1/2 hour at 600°F

Resin Synthesis Scale-Up and Reinforcement Investigation

The large batch of BTDA-DAB-EG resin, designated BED-1 in Section 4.1, was used in this part of the laminating program to demonstrate both the adaptability of scaled-up BTDA-DAB-EG resins to laminating processes as well as the effect of various reinforcement fabrics and finishes on the mechanical strength properties of laminates formed from the BTDA-DAB-EG resin system. The various reinforcements used in this portion of the laminate program included style 181 "E" and "S" glass fabric with both A-1100 and Volan A finishes. In addition to these materials, several laminates were fabricated using heat-cleaned style 581 quartz cloth and a sample of cloth designated 481/38, GB 276 which was submitted by NASA-LRC.

A second scaled up batch of BTDA-DAB-EG resin designated BED-2 (described in Section 4.1) was used toward the latter part of this investigation after batch BED-1 was depleted. This large batch of BED-2 was considered to be the standard resin arrived at during Phase II and was used for all remaining investigations of the BTDA-DAB-EG resin system. Initial studies indicated that the BED-2 resin could be continuously coated on style 181 "E" glass fabric in a coating tower to give a workable prepreg. Several laminates were fabricated successfully with this tower impregnated material. Laminate PF-112 was formed from the tower-coated material using the usual methods followed for prior laminates, while laminate PF-117 was formed using a vacuum bag technique with subsequent postcuring to $700^{\circ}F$ under pressure in a heated press.

Several laminates also were made using PMDA-DAB-EG resin D1516-99 on "E" and "S" glass fabrics with an A-1100 finish to demonstrate that these reinforcements appear to be compatible with the PMDA-DAB-EG system as well as the BTDA-DAB-EG resin system. These laminates were designated PF-115 and PF-116.

The results of the resin synthesis scale up and reinforcement investigation are summarized in Table XIII.

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Table XIII. BTDA-DAB-EG and PMDA-DAB-EG Laminate Properties for Resin Scale Up and Reinforcement Study

Laminate Designation [1]	Resin Designation	Reinforcement (finish)	Laminating Conditions			Final Resin Content, percent		Density, gm/cc		Volume Percent Voids in Resin, percent		Average Flexural Strength, psi x 10⁻³		Average Modulus, psi x 10⁻⁶	
			Contact Time minutes	Maximum Pressure, psi	Temperature Range, °F	As Molded	As Postcured	As Molded	As Postcured	As Molded	As Postcured	Room Temperature	Elevated[8] Temperature	Room Temperature	Elevated[8] Temperature
PF-96	BED-1	Style 181, "E" glass fabric (A1100)	3-1/2[4]	1250	450-680	29.1	-	1.80	-	23.5	-	72.0	47.0	3.60	2.70
PF-97	BED-1	Style 1581, "S" glass fabric (Volan A)	3-1/2[4]	1250	450-680	20.4	-	1.87	-	30.2	-	43.1	-	3.59	-
PF-98	BED-1	Style 1581, "S" glass fabric (heat cleaned)	5[4]	1250	450-680	24.6	-	1.85	-	23.9	-	41.0	-	2.14	-
PF-99	BED-1	Style 181, "E" glass fabric (A1100)	4-1/2[5]	1250	450-680	18.5	-	1.92	-	33.2	-	69.5	-	3.44	-
PF-100	BED-1	Style 181, "E" glass fabric (A1100)	4[5]	400	450-725	27.2	-	1.78	-	28.2	-	68.9	51.7	3.12	2.69
PF-101	BED-1	Style 181, "E" glass fabric (A1100)	3-1/2[5]	600	450-650	31.1	-	1.80	-	20.4	-	65.8	-	3.08	-
PF-102	BED-1	Style 181, "E" glass fabric (A1100)	2-1/2[5]	600	450-680	20.6	-	1.87	-	32.9	-	67.8	-	3.09	-
PF-103	BED-1	Style 181, "E" glass fabric (A1100)	3[5]	400	450-680	23.8	-	1.88	-	25.7	-	68.8	-	2.96	-
PF-104	BED-1	Style 581 Quartz cloth (heat cleaned)	4[4]	400	450-680	24.6	-	1.66	-	43.1	-	24.0	24.7	5.02	5.24
PF-104[3]	BED-1	Style 581 Quartz cloth (heat cleaned)	4[4]	400	450-680	-	21.7	-	1.62	-	50.4	15.6	14.9	4.42	5.06
PF-105	BED-1	Style 181, "E" glass fabric (A1100)	3-1/2[4]	400	450-600	23.6	-	1.91	-	23.3	-	61.7	-	3.00	-
PF-106	BED-1	Style 181, "E" glass fabric (A1100)	3[5]	400	450-700	25.3	-	1.81	-	29.0	-	72.2	-	2.93	-
PF-107	BED-1	Style 181, "E" glass fabric (A1100)	2-1/2[5]	400	450-700	22.9	-	1.82	-	32.5	-	63.7	-	3.13	-
PF-108	BED-1	Style 181, "E" glass fabric (A1100)	2-1/2[5]	400	450-700	22.5	-	1.87	-	29.0	-	71.4	-	3.31	-
PF-109	BED-1	Style 181, "E" glass fabric (A1100)	2[5]	400	450-700	26.2	-	1.83	-	25.7	-	78.4	-	3.42	-
PF-110	BED-1	NASA - Langley 481/38 GB 276	2[5]	400	450-700	22.2	-	1.92	-	21.7	-	72.9	-	3.58	-
PF-111	BED-2	Style 181, "E" glass fabric (A1100)	1-1/2[5]	400	450-700	20.1	-	1.86	-	34.8	-	69.2	-	2.89	-
PF-112[6]	BED-2	Style 181, "E" glass fabric (A1100)	2-1/2[5]	400	450-700	23.7	-	1.85	-	28.5	-	67.8	-	3.22	-
PF-113	BED-2	Style 181, "S" glass fabric (A1100)	2[5]	400	450-700	25.5	-	1.79	-	27.7	-	70.8	-	3.39	-
PF-114	BED-2	Style 181, "E" glass fabric (A1100)	1-1/2[5]	400	450-700	23.0	-	1.85	-	27.0	-	55.0	-	3.58	-
PF-115[2]	D1516-99	Style 181, "E" glass fabric (A1100)	2-1/2[5]	400	450-700	29.2	-	1.80	-	23.5	-	47.8	-	2.71	-
PF-116[2]	D1516-99	Style 181, "S" glass fabric (A1100)	2-1/2[5]	400	450-700	23.7	-	1.81	-	29.2	-	58.4	-	3.44	-
PF-117[6][7]	BED-2	Style 181, "E" glass fabric (A1100)		15	350-500	29.5	22.8	1.51	1.56	44.1	50.8	50.2	-	2.88	-

[1] All laminates were fabricated with BTDA-DAB-EG resin except PF-115 and PF-116
[2] Laminates PF-115 and PF-116 fabricated with PMDA-DAB-EG resin
[3] Laminate postcured to 850°F over 58 hours in argon
[4] Prepreg conditioned at 225°F and "B" staged at 300°F
[5] Prepreg conditioned at 225°F and "B" staged at 400°F
[6] Prepreg coated continuously in a heated coating tower
[7] Vacuum bag laminate
[8] Tested at 600°F after 1/2 hour at 600°F

Laminates for Summary Evaluation of the BTDA-DAB-EG
Resin System

A series of laminates was fabricated with BED-2 resin and style 181 "E" glass as a conclusion to the optimization of the BTDA-DAB-EG resin system. The first two laminates formed were to determine the best processing conditions for lamination with the BED-2 standard resin. The results of flexural strength tests indicated that better strength values would be obtained from laminates which were formed at pressures of approximately 1000 psi and temperatures in the 600^OF range. Post-curing these laminates to 700^OF in argon did not improve the strength values; thus the postcure was discontinued for this last series of laminates. Several laminates also were fabricated in vacuum bags and one with an alumina filled BED-2 resin. These laminates were exposed to elevated temperature aging in air at 600^OF to determine the resin retention properties of BED-2 laminates. The thermal properties of the BTDA-DAB-EG laminates are discussed in greater detail in Section 4.4. A final series of 11 laminates was fabricated, with BED-2 tower-coated "E" glass cloth, and subjected to the tests outlined in Table XIV. The results of thermal testing of these laminates are discussed in Section 4.4 as are the results of electrical tests in Section 4.5.

The remaining laminates not tested for thermal or electrical properties were subjected to the various strength tests "as molded" and after aging at 500^OF in air for either 50 and/or 100 hours. The results of these tests are summarized in Table XV. These results indicate that the BTDA-DAB-EG laminates are considerably more stable to air oxidation at 500^OF than at 600^OF with good retention of strength and modulus even after 100 hours aging.

4.4 THERMAL PROPERTIES

The study of the BTDA-DAB-EG thermal properties included both the determination of resin retention of the laminates when aged

Table XIV. Physical Properties of BTDA-DAB-EG Laminates Tested for Mechanical, Thermal and Electrical Properties

Laminate Designation (1) (2)	Laminating Conditions			Final Resin Content percent	Density, gm/cc	Volume Percent Voids in Resin, percent	Average Flexural Strength, psi x 10^{-3} Room Temperature	Average Modulus, psi x 10^{-6} Room Temperature	Remarks
	Contact Time, minutes	Maximum Pressure, psi	Temperature Range, °F						
PF-120	3 (5)	250	600	23.9	1.69	40.5	61.8	2.73	5% resin retention after 200 hours in air at 600°F
PF-120(3)	3 (5)	250	600	21.5	1.67	46.1	57.1	2.74	-
PF-121	1/4 (6)	1000	600	24.2	1.89	24.0	79.1	3.49	4% resin retention after 200 hours in air at 600°F
PF-121(3)	1/4 (6)	1000	600	21.8	1.84	33.0	63.9	3.41	-
PF-123	- (7)	15	275-440	27.0	1.76	30.1	-	-	27% resin retention after 200 hours in air at 600°F
PF-124	- (7)	3750	275-700	22.6	1.96	21.3	-	-	27% resin retention after 200 hours in air at 600°F
PF-126(4)	- (6)	2500	275-575	34.7	1.83	-	-	-	24% resin retention after 200 hours in air at 600°F
PF-132	1/2 (6)	1000	600	28.7	1.84	20.6	-	-	Tested for tensile strength and modulus at room temperature after aging at 500°F
PF-133	1/2 (6)	1000	600	28.1	1.83	22.8	-	-	Tested for short time dielectric strength at room temperature
PF-134	1/2 (6)	1000	600	30.5	1.80	21.3	-	-	Tested for tensile strength and modulus at room temperature after aging at 500°F
PF-135	1/2 (6)	1000	600	28.2	1.82	23.5	-	-	Tested for thermal conductivity at room temperature
PF-136	1 (6)	1000	550-600	29.0	1.83	21.3	-	-	Tested for short time dielectric strength at room temperature
PF-137	1 (6)	1000	550-600	25.2	1.91	20.6	-	-	Tested for edgewise compressive strength and modulus at room temperature
PF-138	1 (6)	1000	550-600	23.9	1.92	22.1	76.1	4.0	Tested for flexural strength and modulus at room temperature after aging at 500°F
PF-139	1 (6)	1000	550-600	29.9	1.89	14.0	-	-	-
PF-140	1 (6)	1000	550-600	28.7	1.86	19.1	-	-	Tested for arc resistance at room temperature
PF-141	1 (5)	1000	550-600	31.1	1.85	16.2	-	-	-
PF-142	2 (6)	3000	550-600	28.2	1.85	20.6	-	-	Tested for dielectric constant and loss tangent at 9.28 GHz

(1) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish

(2) All laminates were fabricated with BED-2 tower coated prepreg

(3) Laminate was postcured to 700°F over 20 hours in argon

(4) Laminate fabricated were alumina filled BED-2 resin

(5) Prepreg was conditioned at 225°F and "B" staged at 250°F

(6) Prepreg was conditioned at 225°F and "B" staged at 400°F

(7) Prepreg was conditioned at 225°F with no "B" staging

Table XV. Strength Retention of BTDA-DAB-EG Laminates
after Aging in Air at 500°F

Strength Property Determined	Unexposed Specimens (tested at room temperature)	Time of Exposure at 500°F in air (tested at room temperature)	
		50 hours	100 hours
Flexural Strength in 10^3 psi (percent strength retention)	76.1	59.3 (78%)	50.6 (66%)
Flexural Modulus in 10^6 psi (percent strength retention)	4.0	3.9 (97%)	3.4 (85%)
Tensile Strength in 10^3 psi (percent strength retention)	41.8	44.7 (100%)	37.1 (89%)
Tensile Modulus in 10^6 psi (percent strength retention)	3.3	3.3 (100%)	3.2 (97%)
Edgewise Compressive Strength in 10^3 psi (percent strength retention)	33.8	–	21.7 (64%)
Edgewise Compressive Modulus in 10^6 psi (percent strength retention)	3.9	–	3.4 (87%)

at 600°F in forced air and the determination of the thermal conductivity
of a representative specimen from the last series of BTDA-DAB-EG
laminates fabricated. The thermal effects on the mechanical strength
properties at 600°F are scattered throughout Section 4.3 for laminates
prepared at various stages in Phase II. The effect of aging of 500°F
also has been investigated and the results summarized in Table XV.

The effect of aging in air at 600°F for one laminate formed from
BED-1 resin and five laminates formed from BED-2 resin is summa-
rized in Table XVI. The results of these tests indicated poor resin

Table XVI. Thermal Aging Characteristics of BTDA-DAB-EG
Laminates in Air at 600°F

Laminate Designation	Resin Designation	Resin Content, percent	Volume Percent Voids in Resin	Resin Retention at 600°F in Air, percent				
				Hours				
				100	200	300	400	500
PF-109	BED-1	26.2	25.7	48	15	–	–	–
PF-109[1]	BED-1	26.2	25.7	–	91	–	–	–
PF-120	BED-2	23.9	40.5	30	5	–	–	–
PF-121	BED-2	24.2	24.0	26	4	–	–	–
PF-123	BED-2	27.0	30.1	44	27	–	–	–
PF-124	BED-2	22.6	21.3	46	27	14	6	3
PF-126	BED-2 (alumina filled)	34.7	–	51	24	6	–	–
(1) Laminate aged in argon at 600°F								

retention for all laminates tested regardless of the initial resin content, the volume percent voids in the resin matrix or the inclusion of an inert filler into the resin matrix. Examination of Table XVI indicates that all laminates tested lost 50 percent or more of their resin content in 100 hours when aged at 600°F in air. However, a control specimen of PF-109 aged in an argon atmosphere at 600°F showed a resin retention of 91 percent after 200 hours. These results indicate that the BTDA-DAB-EG laminates predominantly undergo oxidative rather than thermal decomposition at 600°F.

In addition to the thermal aging studies the thermal conductivity of laminate PF-135 was determined by the Cenco-Fitch Method. The

results of this transient thermal conductivity test indicated laminate PF-135 to have a k value of 7.8×10^{-4} cal/sec/cm^2/$^\circ$C/cm (0.19 BTU/hr/ft^2/$^\circ$F/ft). This value of thermal conductivity is in the range typical of most glass reinforced polymeric composites.

4.5 ELECTRICAL PROPERTIES

A series of electrical properties was determined for the last set of BTDA-DAB-EG laminates formed at the conclusion of the laminating program. These tests were performed on 12-ply "E" glass reinforced BTDA-DAB-EG laminates following standard A.S.T.M. Test Methods with the exception of the dielectric constant and dissipation factor measurements on laminate PF-142. Laminate PF-142 was formed from 39 plies of tower-coated "E" glass - BED-2 prepreg to enable the dielectric constant and loss tangent to be determined at X-band frequencies. A laminate somewhat thicker than the normal 12-ply laminate was needed so that a specimen could be cut to fit the Hughes resonant cavity dielectrometer. The results of the electrical property measurements are summarized in Table XVII.

The results indicate that the laminates formed from BTDA-DAB-EG resin display electrical properties which would be expected from most glass-reinforced polymeric composites. The one exception is the dissipation factor which indicates that the laminates are somewhat less "lossy" than might be expected. The low loss tangent exhibited by these laminates possibly could be attributed to the relatively high volume percent voids in the resin matrix. Further work is needed on the unreinforced molded resin to either verify or dispel this hypothesis.

4.6 ADDITIONAL STUDIES

To demonstrate the feasibility of forming a laminate in other than a flat shape, a piece of aluminum channel with inside dimensions of 1-1/8 inches wide by 7/16 inches deep was selected as a form. A prepreg was prepared that consisted of 181 glass cloth with an A1100

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Table XVII. Room Temperature Electrical Properties
of BTDA-DAB-EG Laminates

Electrical Property	Test Method	Laminates Tested	Property Values (room temperature)
Surface Resistivity	A. S. T. M. Method D257	PF-135	3.0×10^{14} ohms
Volume Resistivity	A. S. T. M. Method D257	PF-135	2.3×10^{14} ohm-cm
Arc Resistance	A. S. T. M. Method D495	PF-140	206 seconds (tracked)
Dielectric Strength (short time)	A. S. T. M. Method D149	PF-133 PF-135 PF-136	120 volts/mil
Dielectric Constant	A. S. T. M. Method D150	PF-135	4.8 at 1 KH_z 4.5 at 1 MH_z
	Hughes Test Spec. 3-063-5	PF-142	4.65 at 9.28 GH_z
Dissipation Factor	A. S. T. M. Method D150	PF-135	0.001 at 1 KH_z 0.012 at 1 MH_z
	Hughes Test Spec. 3-063-5	PF-142	0.007 at 9.28 GH_z

finish that had been coated with three coats of BTDA-DAB-EG resin
dried at 225°F for 15 minutes after each coating and then "B" staged
at 300°F for 5 minutes.

The prepreg was cut into 2-1/4 x 5-inch plies and an 8-ply layup
was formed in the aluminum channel using FEP Teflon both as a sepa-
rator and as the vacuum bag material. One ply of perforated FEP
Teflon was used on the outside of the part along with three plies of
181 bleeder cloth. The part was vacuum bagged and placed in an oven
at 250°F, the temperature was increased to 450°F in 30 minutes, held
at 450°F for 1 hour and cooled to below 200°F before removal from
the vacuum bag and form.

As the part came out of the vacuum bag the resin content was calculated to be 24.2 percent. Then the part was cut crosswise into two separate parts of approximately the same size. One designated PC-2 was placed in an argon postcure from 275 to 600°F in 48 hours, 2 hours at 600°F and removed below 200°F. The postcured part had a resin content of 19.6 percent, showed a slight amount of warping, had a very hard texture, was black in color, and showed no evidence of delamination. The part which had not been postcured, designated as PC-1, was packaged along with part PC-2 and shipped to NASA-LRC for examination.

In an attempt to determine the finished density of the various types of BTDA-DAB-EG resins, disks were molded from both the diacid diester type (D1516-37) and the tetraester type (D1516-46). The precipitated diacid diester polymer was ground into a fine powder with a mortar and pestle and introduced into a 2-inch diameter mold. A pressure of 12,000 psi was applied; the temperature of the mold was varied from 300°F, for 1 hour, to 350°F, for 1 hour, to 400°F for 2 hours. The mold was cooled to below 200°F, and the cast material removed. The finished molding had a density of 1.38 grams/cc and a Barcol hardness of approximately 50. Since it was shown that this diacid diester type of polymer powder could be molded successfully an attempt was made to mold powder precipitated from the tetraester type resin.

Two 1/2-inch diameter discs were pressed using precipitated tetraester type polymer powder. Both discs were pressed at 12,000 psi. One disk was held in the mold at 300°F for 1 hour and 450°F for 1 hour, allowed to cool to below 200°F, and removed from the mold. This disk had a density of 1.36 gm/cc. The other disc was held in the mold at 450°F for 1 hour, allowed to cool below 200°F and removed from the mold. This disk had a density of 1.30 gm/cc.

Preliminary investigation indicated that the BTDA-DAB-EG resin will form a foam-like material by heating in air at 300°F. A sample of this type resin heated for 4 hours at 300°F formed a foam with a density of approximately 33 pounds per cubic foot.

Subsequent postcuring of this foam from 275 to 600°F produced a hard, tough foam with a density of approximately 26 pounds per cubic foot.

Two filament wound cylinders were molded using both "E" glass and "S" glass rovings for winding. The roving was preimpregnated with resin in a coating tower prior to the filament winding and the winding operation conducted using the preimpregnated roving rather than wet winding with the resin. The glass reinforced resin cylinders were wound on an En-Tec Model 424 filament winding machine in the circumferential mode. Type A NOL test rings were taken from these experimental cylinders according to A.S.T.M. Method D2291 and tested for tensile strength at room temperature and 500°F according to A.S.T.M. Method D2290. The results of these tests are summarized in Table XVIII.

4.7 CONCLUSIONS

The most important conclusions from Phase I and Phase II were that the resins prepared from the esters and the tetraamine in EG were useful for fabricating reinforced composite structures with excellent mechanical strength characteristics. Resins prepared from the dianhydride and the tetraamine in DMAc, on the other hand, failed to provide composites with adequate flexural strength.

Possible reasons for these results have been presented. Deleterious reactions of the polymer with the amide solvents were considered and cannot be excluded. However, the ionic nature of the A-A-A polymer formed in DMAc appeared to be a more important factor. Because of its ionic structure the A-A-A polymer is infusible, and lacking fusibility it does not undergo sufficient flow in processing to yield high-strength composites.

Polymerizations in EG were carried out with both the diester-diacid derivative and the tetraester derivative of the dianhydride. The structures of these esters were not established but were inferred from the methods of synthesis.

Theoretically, polymers derived from the diester-diacid should have the same fundamental structure as the ionic A-A-A polymers

Table XVIII. Physical Properties of Filament Wound BTDA-DAB-EG Resin Cylinders

Cylinder Number	PR-1	PR-2
Resin designation	BED-2	BED-2
Reinforcement type (roving)	20 end "E" glass	12 end "S" glass
Preimpregnated roving resin content (percent)	38	42
Cure cycle ($^\circ$F)	300-700	300-700
NOL ring resin content (percent)	19.3	22.8
NOL ring volume percent voids	45.6	32.6
NOL ring density (gm/cc)	1.74	1.79
NOL ring tensile strength (ASTM D2290) room temperature tests (psi)	108,100	163,800
NOL ring tensile strength (ASTM D2290) 500°F tests (psi)	89,500	147,700

obtained in DMAc; nevertheless, they exhibited much better laminating characteristics. Two reasons may be given for the improved behavior in EG. First, the actual monomers were changed as well as the solvent; this substantially decreased the rate and extent of reaction. The dianhydride is extremely reactive toward amines; consequently, high polymers are obtained at room temperature. DMAc also is a sufficiently strong solvent to retain these polymers in solution so that high molecular weights can be more readily achieved. A high molecular weight ordinarily would be desirable, but a combination of high molecular weight and ionic character makes the A-A-A polymer obtained in DMAc

infusible. When the reaction is conducted in EG, the diester-diacid (which is the actual monomer) is far less reactive than the anhydride from which it was derived. Higher temperatures are required to induce polymerization with the polymer precipitating from EG before high molecular weights are attained. Although an ionic A-A-A polymer may still be obtained, it probably has a relatively low molecular weight and consequently is still fusible. Polymerization ceases when the reaction mixture is cooled to room temperature. Therefore, the A-A-A polymers obtained in EG probably are more desirable because they have lower molecular weights than similar polymers prepared in DMAc.

A second factor may be the EG or the EG-derived moieties which appeared to be bound to the A-A-A polymer. These moieties would have a plasticizing effect on the polymer and would promote flow.

An additional factor is that most of the polymers prepared in DMAc were PMDA-DAB polymers, while the polymers synthesized in EG were primarily BTDA-DAB materials. The additional single bonds of BTDA also should promote flow in processing.

Polymers prepared from DAB and the BTDA-EG tetraester were not ionic and, therefore, were readily fusible under processing conditions. If the sketchy analytical data are given credence, the actual structure of these polymers deviates considerably from the theoretical structure, but this does not detract from the performance of the cured materials.

The improved strength characteristics of laminates formed in Phase II of the program with BTDA-DAB-EG resins verified the expected improvement in flow characteristics. This increased flow which enabled the formation of higher quality laminates is attributed to (1) the internal bonding of the solvent (which acts as a plasticizer) and (2) the increased molecular flexibility of the polymer formed from BTDA.

While the maximum room temperature flexural strength of Phase I laminates were on the order of 40,000 psi, it was found that room temperature flexural strengths as high as 80,000 psi could be reached with the BTDA-DAB-EG resin system and strengths above 70,000 psi were

achieved on a routine basis. The maximum moduli in Phase I were on the order of 3×10^6 psi while it was demonstrated that moduli above 5×10^6 psi could be achieved with the BTDA-DAB-EG resin system.

The high modulus may be of a great importance to the aerospace industry. In many design applications the stiffness of a material is of far greater importance than its ultimate strength.

It was observed that the volume percent voids in the resin of Phase I laminates were generally in the 40 to 60 percent range and the density of the laminates ranged between 1.46 and 1.82 gm/cc. These high voids and relatively low densities are attributed to loss of volatile components from the laminates during the curing procedure. In Phase II it was found that the increased strength properties were accompanied by a reduction in voids to the 15 to 25 percent range during the latter part of the laminate optimization program, while the densities of corresponding laminates were generally in the 1.80 to 1.95 gm/cc range. These observations of void content and densities along with improved strengths indicate that increased flow characteristics have been achieved while the effects of the loss of volatile components have been minimized.

Despite the greatly improved mechanical strength values and physical properties, the thermal stability of the BTDA-DAB-EG resin laminates were disappointing. Exposure at 600°F in air degraded those laminates tested, such that 50 percent or more of the resin burned off in 100 hours. The degradation was oxidative rather than thermal as proven by a control laminate which retained 91 percent of the resin matrix when exposed to the same temperature conditions in an argon atmosphere for 200 hours. The brief study undertaken as Phase III, however, illustrated that the thermal stability of the BTDA-DAB resin system could be improved to some degree by proper selection of the alcohol used in the formation of the ester intermediate.

The versatility and adaptability of the BTDA-DAB-EG resin system were aptly demonstrated by the vacuum bag formation of flat laminates and deep drawn shapes, intermediate density foams, and high strength filament wound cylinders.

5.0 PHASE III - POLYMERS FROM TETRAETHYL ESTERS

Phase III was initiated as a brief study to determine whether the poor oxidative stability of the BTDA-DAB-EG resin system could be circumvented by substitution of an alternate hydroxy compound in the ester intermediate of the resin system. Several of the syntheses to form the BTDA-DAB-EtOH resin system are described in Section 5.1. No attempt was made at detailed chemical characterization of the resin system. The evaluation of this resin system was based on the physical properties of the laminates described in Section 5.2 and their thermal behavior which is described in Section 5.3. The conclusions are presented in Section 5.4.

5.1 POLYMER SYNTHESIS

During the initial synthesis of the BTDA-DAB-EG tetraester type resins, an attempt was made also at synthesizing a resin from the tetraester formed by the reaction of ethanol and BTDA under similar conditions to those used for the formation of the ethylene glycol tetraester of BTDA.

Since EG has a very low volatility and is lost only very slowly during laminating, it was thought advisable to compare the BTDA-DAB resins prepared in EG with similar resins prepared in a more volatile alcohol. Therefore, resin was synthesized from DAB and an ester that presumably was tetraethyl 3,3',4,4'-benzophenonetetracarboxylate, the BTDA-ethanol tetraester. However, since polymers are quite insoluble in ethanol, the polymer had to be synthesized in essentially a melt of the monomers with some residual ethanol.

The BTDA-ethanol ester was prepared by adding 96.6 grams (0.3 mole) of BTDA to 500 ml of hot absolute ethanol with subsequent dropwise addition of 20 ml of concentrated sulfuric acid. Upon adding the acid, the BTDA went into solution and the reaction mixture was stirred at reflux for 20 hours. The ethanol then was distilled from the reaction vessel until the temperature above the reaction mixture rose above 100°C. The volume of the reaction mixture at this point was

approximately one-third the original volume. The resultant crude mixture was taken up in ether, washed several times with water, and then shaken with 10 percent sodium bicarbonate solution until acidification of the bicarbonate washes failed to produce a precipitate. The ethereal solution then was dried over anhydrous magnesium sulfate. Finally, the ether was evaporated and a product weighing 89.3 gm was collected (63 percent of theoretical).

The BTDA-DAB-EtOH resin was prepared by mixing 89.3 gm (0.19 mole) of the prepared ester with 500 ml of absolute ethanol, heating to reflux under argon and adding 40.5 gm (0.19 mole) of solid DAB. This mixing produced a slurry which was stirred vigorously. Excess ethanol was distilled out of the reaction mixture and the temperature was allowed to rise to $150^{\circ}C$, at which point the mixture became a viscous melt. The temperature kept at $150^{\circ}C$ for 15 minutes, then raised to approximately $200^{\circ}C$. After 90 minutes at these conditions, the mixture became too viscous to be stirred, and the reaction was discontinued. On cooling, the melt became a brittle glass weighing 108.4 gm. DMAc and DMF are solvents for the resin and can be used to prepare a solution. These solvents may be more satisfactory with the esterified polymer than they were with the A-A-A polymers prepared in the amide solvents.

As work progressed through the Phase II program and it became obvious that the BTDA-DAB-EG laminates lacked stability to oxidative degradation, it was decided to study briefly the thermal stability characteristics of the BTDA-DAB-EtOH resin system. Since much of the synthetic chemistry was similar to the ethylene glycol resin system, and the synthesis of a BTDA-DAB-EtOH resin had been accomplished successfully earlier in the program, several more batches of this type resin were synthesized with slight modifications in the original procedure.

A typical synthesis of a BTDA-DAB-EtOH resin is that of resin batch D1516-100A. Since the synthesis of this resin is typical for preparing this type resin and since this resin was used to prepare

laminate PF-131 for the thermal aging studies of the BTDA-DAB-EtOH laminates, it will be described in detail.

The BTDA-EtOH ester was prepared by adding a 955.7 gm (3.0 mole) quantity of BTDA to 4000 ml of ethanol and heating the slurry to reflux. After the BTDA had dissolved, 180 ml of concentrated sulfuric acid was added dropwise, with constant stirring. The mixture was stirred at reflux for 64 hours. Then excess ethanol was distilled off until the volume of reactants was reduced to about 1/3 of the original volume. The crude product was taken up in 3 liters ether and washed 3 times with water. Then it was washed with equal volumes of saturated aqueous sodium bicarbonate until acidification of the bicarbonate washes failed to precipitate carboxyl salts. The partially esterified product from the bicarbonate wash was recovered by total acidification and taken up in ether.

Both fractions of ester in the ether solutions were dried over anhydrous magnesium sulfate, and the ether from each was distilled off after filtering out the magnesium sulfate. Residual solvents in both ester fractions then were removed under vacuum on a rotary still at 150°C for 3 hours. The carboxyl equivalents for both fractions of the ester were determined. The low carboxyl ester fraction had a 0.2 equivalent percent carboxyl and weighed 701.5 gm (50 percent of theoretical). The high carboxyl ester fraction had 23.3 equivalent percent carboxyl and weighed 215.3 gm.

The D1516-100A resin was prepared from this ester by the following synthetic procedure. A 0.38 molar mixture of 141.1 gm of D1516-100 low carboxyl ester with 35.2 gm of D1516-100 high carboxyl ester was heated to 190°C under argon, and 81.7 gm (0.38 mole) of solid DAB was added to the stirred ester. The system was evacuated periodically to remove the ethanol evolved during the reaction. The reaction was continued for 100 minutes at 180°F. The mixture then was cooled in an ice bath and liquid nitrogen was poured over the resulting glass to shatter it into small particles. The product was ground to a powder in a mortar and pestle.

5.2 LAMINATING AND PHYSICAL PROPERTIES

A series of nine laminates was formed using BTDA-DAB-EtOH resins synthesized in different batches. The initial two laminates were fabricated with a BTDA-DAB-EtOH resin dissolved in acetone and the remaining seven laminates were formed as powder layups. The acetone solution of the resin was not used after the initial studies because the solvent appeared to alter the resin system in such a manner that the laminates formed from the solution underwent extreme degradation at elevated temperatures in air.

The laminates formed from the resin powders demonstrated thermal stability superior to the BTDA-DAB-EG laminates. The processing conditions and physical properties of the BTDA-DAB-EtOH laminates are summarized in Table XIX. Examination of Table XIX indicates that flexural strengths above 70,000 psi and moduli above 3×10^6 psi can be achieved easily with laminates formed from the BTDA-DAB-EtOH resin system. The thermal aging studies described in Section 5.3 also indicate thermal stabilities superior to the BTDA-DAB-EG laminates also are readily achieved.

5.3 THERMAL PROPERTIES

Sections of the laminates formed by the procedures described in Section 5.2 were subjected to aging in air at 600°F. By supporting specimens of approximately 6 square inches in a position such that hot air within a forced draft oven was in contact with all surfaces, it was thought that meaningful thermal stability data could be obtained.

A 3/4 inch pellet of the D1516-97D tetraethyl ester type resin was molded for comparison purposes. This is the same resin used to form laminate PF-125, a direct comparison could thus be made between the same resin in the molded condition and as it is used in a laminate. The resin retention properties of the pellet are included in Table XX along with the resin retention properties of the BTDA-DAB-EtOH laminates subjected to isothermal aging in air at 600°F.

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Table XIX. Physical Properties and Processing Conditions
for BTDA-DAB-EtOH Laminates

Laminate Designation [1]	Resin System	Resin Designation	Resin Advancement	Laminating Conditions			Final Resin Content, percent	Density gm/cc	Volume Percent Voids in Resin, percent	Average Flexural Strength, psi x 10^{-3}	Average Modulus, psi x 10^{-6}
				Contact Time minutes	Maximum Pressure, psi	Temperature Range, °F					
PF-118	BTDA-DAB-EtOH (in acetone)	D1516-87	Prepreg dried 30 minutes at 160°F in air	-	200	275-500	18.5	1.86	38.3	63.0	3.42
PF-119	BTDA-DAB-EtOH (in acetone)	D1516-87	Prepreg dried 30 minutes at 160°F in air	-	200	275-500	20.0	1.85	36.2	73.9	3.43
PF-119[2]	BTDA-DAB-EtOH (in acetone)	D1516-87	Prepreg dried 30 minutes at 160°F in air	-	200	275-500	17.8	1.82	43.0	61.1	3.28
PF-122	BTDA-DAB-EtOH	D1516-97D	Resin powder used as received	-	250	275-500	20.0	1.93	28.9	50.8	3.71
PF-122[2]	BTDA-DAB-EtOH	D1516-97D	Resin powder used as received	-	250	275-500	17.0	1.84	43.3	56.7	3.54
PF-125	BTDA-DAB-EtOH	D1516-97D	Resin heated for 30 minutes at 500°F in vacuum	-	2500	400-700	31.4	1.67	30.0	(4)	(4)
PF-127	BTDA-DAB-EtOH	D1516-97F	Resin heated for 20 minutes at 400°F in vacuum	5	2500	450-700	34.0	1.74	21.3	(4)	(4)
PF-127[3]	BTDA-DAB-EtOH	D1516-97F	Resin heated for 20 minutes at 400°F in vacuum	5	2500	450-700	33.6	1.69	25.9	(4)	(4)
PF-128	BTDA-DAB-EtOH	E1706-6	Resin heated for 30 minutes at 430°F in vacuum	5	7000	500-700	28.5	1.72	30.9	(4)	(4)
PF-129	BTDA-DAB-EtOH	D1516-97F	Resin heated for 30 minutes at 430°F in vacuum	10	15,000	500-700	31.2	1.67	30.7	(4)	(4)
PF-130	BTDA-DAB-EtOH	D1516-97F	Resin heated for 45 minutes at 430°F in vacuum	4	7000	500-700	46.5	1.62	16.2	(4)	(4)
PF-131	BTDA-DAB-EtOH	D1516-100A	Resin heated for 35 minutes at 450°F in vacuum	1	4500	550-700	46.3	1.60	18.4	(4)	(4)

(1) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish
(2) Laminate was postcured to 700°F over 20 hours in argon
(3) Laminate was postcured for 5 hours in vacuum at 440°F and 5 minutes at 750°F in air
(4) Laminates not tested for flexural strength or modulus - subjected to isothermal aging in air at 600°F

The thermal properties of both "as molded" and postcured sections of laminates PF-122 and PF-127 are included in Table XX. In addition to the 600°F air aging of laminate PF-131, a specimen of this same laminate was subjected to isothermal aging at 700°F for purposes of comparative degradation rates.

Examination of Table XX and comparison with the thermal aging properties of the BTDA-DAB-EG laminates summarized in Table XVI demonstrates the marked increase in thermal stability of the BTDA-DAB-EtOH laminates. Many of the latter laminates presented in Table XX demonstrate resin retention close to 50 percent after 300 hours aging in air at 600°F while none of the BTDA-DAB-EG laminates retained 50 percent after 100 hours aging time. This was not the case, however, for the BTDA-DAB-EtOH laminates used as acetone solutions. These laminates lost practically all their resin in a matter of 200 hours, thus they demonstrated no improvement over the BTDA-DAB-EG resin system.

In addition to the laminate study, a specimen of BTDA-DAB-EtOH resin D1516-100A was cured in argon and subjected to thermogravimetric analysis. The contour of the thermogram paralleled that of the cured BED-2 thermogram illustrated in Figure 5. Despite the similar behavior of the BTDA-DAB-EtOH resin under TGA analysis, it appeared to be a more thermally stable laminating resin. For this reason, care must be taken in basing the thermal stability of a resin solely on TGA analysis.

Infrared absorption analysis was run on a nominal 1 mil thick film of BTDA-DAB-EtOH resin D1516-100A. The resin powder was advanced for 35 minutes at 450°F, ground to pass a #80 U.S. Standard Sive and pressed between two sheets of Teflon in a press heated to 500°F. The resin was held at contact pressure for 1/2 hour at 500°F, cooled to room temperature and stripped from the Teflon as a film of nominal 1 mil thickness. The infrared absorption spectrum of this cured film is shown in Figure 8. After the spectrum of the cured film had been run, the film was postcured from 300 to 700°F in an argon atmosphere and another infrared spectrum was obtained. The infrared spectrum of this postcured BTDA-DAB-EtOH resin film is shown in Figure 9.

Table XX. Thermal Aging Characteristics of BTDA-DAB-EtOH
Laminates in Air at 600°F

Laminate Designation	Resin Designation	Resin Content, percent	Volume Percent Voids in Resin	Resin Retention at 600°F in Air, percent				
				Hours				
				100	200	300	400	500
Molded Pellet	D1516-97D	100	-	89	77	66	56	45
PF-122	D1516-97D	20.0	28.9	51	32	-	-	-
PF-122[1]	D1516-97D	17.0	43.3	61	39	-	-	-
PF-125	D1516-97D	31.4	30.0	60	35	18	8	-
PF-127	D1516-97F	34.0	21.3	75	49	27	16	10
PF-127[1]	D1516-97F	33.6	25.9	78	47	27	16	11
PF-128	E1706-6	28.5	30.9	88	70	40	20	1
PF-129	E1706-6	31.2	30.7	73	59	44	32	21
PF-130	D1516-97F	46.5	16.2	92	75	53	36	23
PF-131	D1516-100A	46.3	18.4	85	65	46	29	18
PF-131[2]	D1516-100A	46.3	18.4	14	0	-	-	-

[1]Postcured laminates

[2]Laminate aged at 700°F in air

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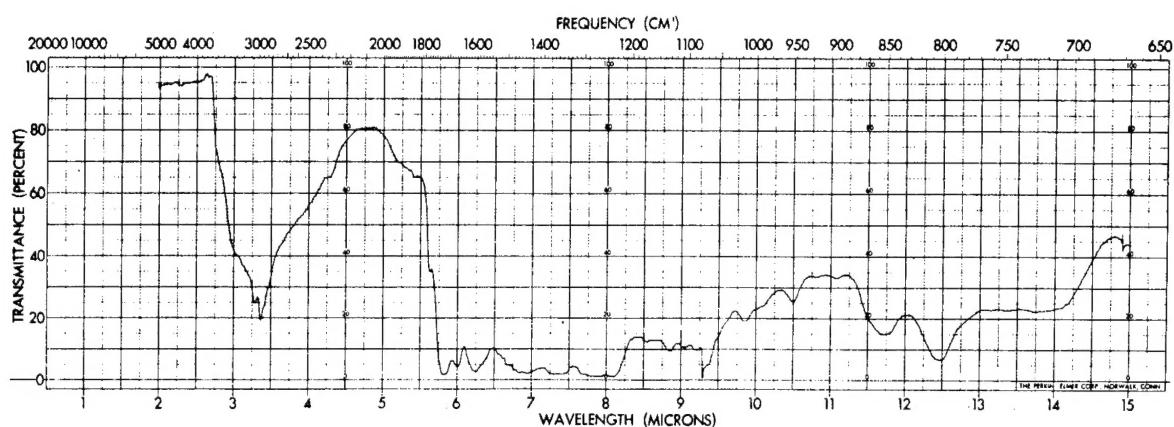
Figure 8.   Infrared Spectrum of Cured BTDA-DAB-EtOH Resin
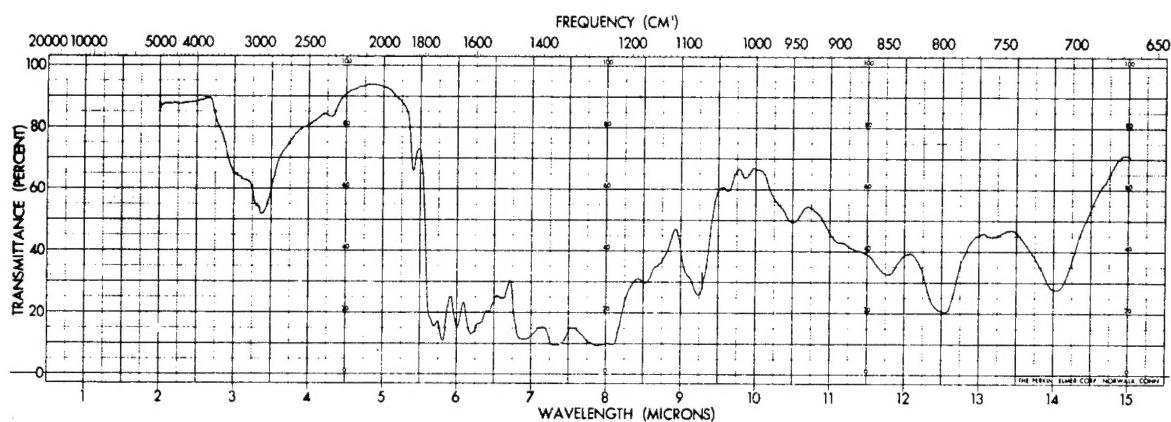
Figure 9.   Infrared Spectrum of Postcured BTDA-DAB-EtOH Resin

Examination of Figures 8 and 9 indicates that a high degree of imide character was attained in both the cured and postcured films; it also indicates the presence of some imidazopyrrolone structure in the postcured condition.   The 1775 cm^{-1} shoulder and 1720 cm^{-1} bands attributed to the imide structure are evident in both the cured and postcured resin resin spectra.   There is a slight shoulder at 1735 cm^{-1} in the spectrum of the cured film.   This may be indicative of the imidazopyrrolone structure; however, the 1760 cm^{-1} and 1620 cm^{-1} bands are not observed so there is no confirmation.   In the spectrum of the postcured resin (Figure 9), a strong band at 1760 cm^{-1} assigned to the Pyrrone carbonyl is observed.   In addition to this carbonyl band, a strong band at 1615 cm^{-1} attributed to the C = N stretch is observed.

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These observations indicate that a high degree of imide character is present in the cured and postcured BTDA-DAB-EtOH resin, as it was in the BTDA-DAB-EG resins. However, there is a good indication that some imidazopyrrolone character is developed during the 700°F postcure of the BTDA-DAB-EtOH resin.

5.4 CONCLUSIONS

A brief investigation of the BTDA-DAB-EtOH resin system indicates that laminates with flexural strengths above 70,000 psi and moduli above 3×10^6 psi can be achieved readily. These mechanical strength values are comparable to many of the BTDA-DAB-EG laminates fabricated. In addition to the comparable mechanical strength properties of the BTDA-DAB-EtOH laminates, they demonstrate stability to air oxidation superior to the BTDA-DAB-EG laminates.

The thermogravimetric analysis of a cured BTDA-DAB-EtOH resin indicates that the thermal stability of this resin system should be very similar to that of the cured BTDA-DAB-EG, but this is contradicted by the superior thermal stability of laminates formed from the BTDA-DAB-EtOH resin system.

The infrared spectra of cured and postcured BTDA-DAB-EtOH resin indicates a high degree of imide character present with some evidence for the presence of the imidazopyrrolone structure in the postcured condition.

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